

HAROLD A. WITTCOFF • BRYAN G. REUBEN • JEFFREY S. PLOTKIN

Industrial Organic Chemicals

THIRD EDITION

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INDUSTRIAL ORGANIC CHEMICALS

Other Books by the Authors

The Phosphatides, by Harold A. Wittcoff, Reinhold, New York, 1950.

The Chemical Economy, by Bryan G. Reuben and Michael L. Burstall, Longman, London, 1973.

Industrial Organic Chemicals in Perspective; Part 1: Raw Materials and Manufacture, Part 2: Technology, Formulation, and Use, by Bryan G. Reuben and Harold A. Wittcoff, Wiley, New York, 1980.

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Bread: A Slice of History, by John S. Marchant, Bryan G. Reuben, and Joan P. Alcock, The History Press, Stroud, Gloucestershire, 2008.

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Harold A. Wittcoff

Scientific Adviser, Nexant ChemSystems Inc. (retired)

Vice President of Corporate Research, General Mills, Inc. (retired)

Bryan G. Reuben

Professor Emeritus of Chemical Technology

London South Bank University

Jeffrey S. Plotkin

Director, Process Evaluation and Research Planning Program

Nexant ChemSystems Inc.



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*To our wives, Dorothy, Catherine, and Marisa, children,
grandchildren, and great-grandchildren.*

CONTENTS

Preface	xxiii
Preface to the First Edition	xxv
Preface to the Second Edition	xxvii
Acknowledgments	xxix
Bryan Godel Reuben 1934–2012	xxxi
List of Acronyms and Abbreviations	xxxiii
Introduction: How to Use <i>Industrial Organic Chemicals, Third Edition</i>	1
I.1 Why This Book Was Written and How It Is Structured	2
I.2 North American Industry Classification System	5
I.3 Units and Nomenclature	5
I.4 General Bibliography	6
I.4.1 Encyclopedias	6
I.4.2 Books	7
I.4.3 Journals	8
I.4.4 Patents	9
I.4.5 Statistics and Internet Sources of Information	10
1. The Evolution of the Organic Chemicals Industry	13
1.1 The National Economy	13
1.2 Size of the Chemical Industry	16
1.3 Characteristics of the Chemical Industry	22
1.3.1 Capital Intensity and Economies of Scale	22
1.3.2 Criticality and Pervasiveness	24
1.3.3 Freedom of Market Entry	26
1.3.4 Strong Regulation	27
1.3.4.1 European Legislation	29
1.3.4.2 Political Factors	30
	vii

1.3.5	High but Declining Research and Development Expenditures	34
1.3.6	Dislocations	41
1.4	The Top Companies	43
1.5	The Top Chemicals	44
	Endnotes	46
2.	Globalization of the Chemical Industry	49
2.1	Overcapacity	51
2.1.1	Economic Cycles	55
2.2	Restructuring, Mergers, and Acquisitions	56
2.2.1	SuICide of a UK Company	60
2.2.2	Private Equity	61
2.3	Participation in International Trade	63
2.4	Competition from Developing Countries	66
	Endnotes	69
3.	Transporting Chemicals	71
3.1	Shipping Petroleum	71
3.2	Shipping Gas	74
3.3	Shipping Chemicals	75
3.3.1	Gases	75
3.3.2	Liquids	77
3.3.3	Solids	85
3.4	Health and Safety	86
3.5	Economic Aspects	87
3.6	Trade in Specific Chemicals	88
3.7	Top Shipping Companies	90
	Endnotes	91
4.	Chemicals from Natural Gas and Petroleum	93
4.1	Petroleum Distillation	97
4.2	Shale Gas	100
4.2.1	Shale Gas Technology	101
4.3	Naphtha Versus Gaseous Feedstocks	102

4.4	Heavier Oil Fractions	103
4.5	Steam Cracking and Petroleum Refining Reactions	104
4.5.1	Steam Cracking	106
4.5.2	Choice of Feedstock	108
4.5.3	Economics of Steam Cracking	110
4.6	Catalytic Cracking	114
4.7	Mechanisms of Steam and Catalytic Cracking	117
4.8	Catalytic Reforming	119
4.9	Oligomerization	122
4.10	Alkylation	124
4.11	Hydrotreating and Coking	125
4.12	Dehydrogenation	126
4.13	Isomerization	128
4.14	Metathesis	128
4.14.1	Metathesis Outside the Refinery	129
4.14.2	Mechanism of Metathesis	131
4.15	Function of the Refinery and the Potential Petroleum Shortage	133
4.15.1	Unleaded Gasoline and the Clean Air Act	134
4.16	Separation of Natural Gas	136
4.17	Oil from Tar Sands	137
	Endnotes	137
5.	Chemicals and Polymers from Ethylene	139
5.1	Ethylene Polymers	141
5.1.1	Discovery of Low and High Density Polyethylenes	142
5.1.2	Low Density Polyethylene	144
5.1.3	High Density Polyethylene	146
5.1.4	Linear Low Density Polyethylene	147
5.1.5	Very High Molecular Weight Polyethylene	148
5.1.6	Metallocene Polyethylenes	149
5.1.7	Very Low Density Polyethylene	149
5.1.8	Bimodal HDPE	149
5.1.9	“Green” Polyethylene	150

5.2	Ethylene Copolymers	151
5.2.1	Chlorosulfonated Polyethylene	151
5.2.2	Ethylene-Vinyl Acetate	151
5.2.3	Ionomers	152
5.2.4	Copolymer from “Incompatible” Polymer Blends	152
5.2.5	Ethylene–Propylene Elastomers	153
5.2.6	Polyolefin Elastomers	153
5.3	Oligomerization	154
5.3.1	Dimerization	154
5.3.2	Ziegler Oligomerization of Ethylene	155
5.3.3	Other Ethylene Oligomerization Technologies	156
5.3.4	Shell Higher Olefins Process (SHOP)	158
5.4	Vinyl Chloride	160
5.5	Acetaldehyde	165
5.6	Vinyl Acetate	167
5.7	Ethylene Oxide	169
5.7.1	Ethylene Glycol	171
5.7.2	Proposed Non-Ethylene Oxide Processes for Ethylene Glycol Production	174
5.8	Styrene	177
5.9	Ethanol	181
5.10	Major Chemicals from Ethylene – A Summary	182
5.11	Lesser Volume Chemicals from Ethylene	185
5.11.1	Hydroformylation – Propionaldehyde, Propionic Acid, and <i>n</i> -Propanol	185
5.11.2	Ethyl Halides	186
5.11.3	Acetaldehyde Chemistry	187
5.11.4	Metal Complexes	191
5.11.5	Ethylenediamine and Related Compounds	191
5.11.6	Ethylene Oxide and Ethylene Glycol Derivatives	193
5.11.6.1	Oligomers	193
5.11.6.2	Glycol Ethers and Esters	194
5.11.6.3	Ethylene Carbonate	197
5.11.6.4	Aminoethyl Alcohols (Ethanalamines) and Derivatives	198
5.11.6.5	Ethyleneimine	199

5.11.6.6	1,3-Propanediol	200
5.11.6.7	Ethylene Glycol Derivatives	201
5.11.7	Vinyl Chloride and Ethylene Dichloride Derivatives	203
5.11.8	Vinyl Fluoride and Vinylidene Fluoride	204
5.11.9	Ethylene Dibromide	205
5.11.10	Ethanol Derivatives	206
5.11.11	Vinyl Esters and Ethers	207
Endnotes		208
6. Chemicals and Polymers from Propylene		211
6.1	On-Purpose Propylene Production Technologies and Propane Dehydrogenation	214
6.1.1	Propylene Via Enhanced Fluidized Catalytic Cracking	215
6.1.2	Propylene Via Selective C ₄ /C ₅ Cracking	215
6.2	Main Polymers and Chemicals from Propylene	217
6.2.1	Propylene Polymers and Copolymers	217
6.3	Oligomerization	221
6.4	Acrylic Acid	222
6.4.1	Biorenewable Processes to Acrylic Acid	225
6.4.2	Acrylic Acid Markets	226
6.5	Acrylonitrile	227
6.5.1	Uses of Acrylonitrile	230
6.6	Cumene/Phenol and Cumene Hydroperoxide	231
6.7	Acetone and Isopropanol	233
6.7.1	Methyl Methacrylate	235
6.7.2	Methyl Isobutyl Ketone and Other Acetone Derivatives	242
6.8	Propylene Oxide	242
6.8.1	Other Propylene Oxide Processes	247
6.8.1.1	Acetoxylation of Propylene	248
6.8.1.2	Direct Oxidation	249
6.8.1.3	Use of Peracids	249
6.8.1.4	Electrochemical Processes	250
6.8.1.5	Biotechnological Approaches	252
6.8.2	Propylene Oxide Applications	253

6.9	<i>n</i> -Butyraldehyde and Isobutyraldehyde	255
6.9.1	Uses for Butyraldehyde, Isobutyraldehyde, and <i>n</i> -Butanol	258
6.9.2	Other Oxo Products	260
6.10	Major Chemicals from Propylene – A Perspective	261
6.11	Lesser Volume Chemicals from Propylene	263
6.11.1	Allyl Chloride and Epichlorohydrin	263
6.11.2	Glycerol	266
6.11.3	Acrylamide	266
6.11.4	Acrolein	268
6.11.5	Acrylonitrile Derivatives	270
	Endnotes	270
7.	Chemicals from the C₄ Stream	273
7.1	Chemicals and Polymers from Butadiene	277
7.1.1	Tires	280
7.1.2	Styrene–Butadiene Elastomers	281
7.1.3	Polybutadienes and Other Elastomers	282
7.1.4	Acrylonitrile–Butadiene–Styrene Resins	283
7.1.5	Hexamethylenediamine	284
7.1.6	Lesser Volume Chemicals from Butadiene	289
7.1.6.1	Cyclization	289
7.1.6.2	Dimerization and Trimerization	291
7.1.6.3	Diels–Alder Reactions	293
7.1.6.4	Adipic Acid	294
7.1.6.5	1,4-Butanediol	294
7.1.6.6	<i>trans</i> -1,4-Hexadiene	295
7.1.6.7	Dimethyl-2,6-naphthalene Dicarboxylate	295
7.1.6.8	Butadiene Monoepoxide	296
7.2	Chemicals and Polymers from Isobutene	296
7.2.1	Methyl <i>tert</i> -Butyl Ether	297
7.2.2	Butyl Rubber	298
7.2.3	Polyisobutenes and Isobutene Oligomers and Polymers	298
7.2.4	<i>tert</i> -Butanol	299
7.2.5	Methyl Methacrylate	299
7.2.6	Lesser Volume Chemicals from Isobutene	299

7.3	Chemicals and Polymers from 1- and 2-Butenes	302
7.4	Chemicals from <i>n</i> -Butane	303
7.4.1	Acetic Acid	303
7.4.2	Maleic Anhydride	303
7.4.3	Succinic, Malic, Fumaric, and Tartaric Acids	306
	Endnotes	307
8.	Chemicals from the C₅ Stream	309
8.1	Separation of the C ₅ Stream	311
8.2	Isoprene	312
8.2.1	Natural Rubber	312
8.2.2	Vulcanization	313
8.2.3	Production of Petrochemical Isoprene	314
8.2.4	Applications of Isoprene	317
8.3	Cyclopentadiene and Dicyclopentadiene	319
8.4	Pentene-1 and Piperylene	321
	Endnotes	321
9.	Chemicals from Benzene	323
9.1	Phenol	326
9.1.1	Phenolic Resins	331
9.1.2	Bisphenol A	333
9.1.2.1	Epoxy Resins	333
9.1.2.2	Polycarbonate Resins	334
9.1.2.3	Lesser Volume Uses for Bisphenol A	337
9.1.2.4	Environmental Problems	340
9.1.3	Cyclohexanone	341
9.1.4	Alkylphenols	342
9.1.5	Chlorinated Phenols	342
9.1.6	2,6-Xylenol/Cresols	343
9.1.7	Aniline from Phenol	344
9.2	Cyclohexane	344
9.2.1	Adipic Acid	344
9.2.1.1	Nylons from Adipic Acid	349
9.2.2	Caprolactam	349

9.3	Aniline	354
9.3.1	4,4'-Diphenylmethane Isocyanate	357
9.4	Alkylbenzenes	361
9.5	Maleic Anhydride	362
9.6	Chlorinated Benzenes	363
9.7	Dihydroxybenzenes	364
9.7.1	Hydroquinone	364
9.7.2	Resorcinol	368
9.7.3	Catechol	369
9.8	Anthraquinone	370
9.8.1	Hydrogen Peroxide	371
	Endnotes	372
10.	Chemicals from Toluene	375
10.1	Hydrodealkylation, Disproportionation, and Transalkylation	375
10.2	Solvents	378
10.3	Dinitrotoluene and Toluene Diisocyanate	378
10.4	Lesser Volume Chemicals from Toluene	380
	Endnotes	382
11.	Chemicals from Xylenes	383
11.1	<i>o</i> -Xylene and Phthalic Anhydride	386
11.1.1	Plasticizers	387
11.1.2	Alkyd Resins	391
11.1.3	Unsaturated Polyester Resin	393
11.2	<i>m</i> -Xylene and Isophthalic Acid	395
11.2.1	Uses of Isophthalic Acid	396
11.3	<i>p</i> -Xylene and Terephthalic Acid/Dimethyl Terephthalate	397
11.3.1	Oxidation of <i>p</i> -Xylene	398
11.3.2	Alternate Sources for Terephthalic Acid	400
11.3.3	Poly(ethylene terephthalate)	400
11.3.4	Lower Volume Polymers from Terephthalic Acid	403
	Endnotes	404

12. Chemicals from Methane	407
12.1 Hydrocyanic Acid	408
12.2 Halogenated Methanes	411
12.2.1 Chloromethane	412
12.2.2 Dichloromethane	413
12.2.3 Trichloromethane	413
12.2.4 Fluorocarbons	414
12.2.5 Tetrachloromethane and Carbon Disulfide	414
12.2.6 Bromomethane	416
12.3 Acetylene	417
12.3.1 1,4-Butanediol and 2-Methyl-1,3-propanediol	419
12.3.2 Lesser Uses for Acetylene	423
12.4 Synthesis Gas	424
12.4.1 Steam Reforming of Methane	425
12.4.2 Variants of Steam Reforming	427
12.4.3 Partial Oxidation of Hydrocarbons	428
12.4.4 Solid Feedstocks	428
12.4.5 Hydrogen	429
12.5 Chemicals from Synthesis Gas	429
12.5.1 Ammonia and Its Derivatives	430
12.5.1.1 The Crisis of Nitrogen Depletion	430
12.5.1.2 Ammonia Manufacture	431
12.5.1.3 Urea and Melamine Resins	434
12.5.2 Methanol	435
12.5.2.1 Formaldehyde	438
12.5.2.2 Acetic Acid	439
12.5.2.3 Acetic Anhydride	442
12.5.2.4 Methanol to Gasoline	445
12.5.2.5 Methanol to Olefins	446
12.5.2.6 Lower Volume and Proposed Uses for Methanol	448
12.5.2.7 C ₁ -Based Development Processes	452
12.6 Carbon Monoxide Chemistry	454
12.6.1 Proposed Chemistry Based on Carbon Monoxide	455
12.7 Gas-to-Liquid Fuels	459
12.7.1 Sasol GTL Technology	459
12.7.2 Shell Middle Distillate Synthesis	459

12.7.3	Other GTL Technologies	460
	Endnotes	460
13.	Chemicals from Alkanes	463
13.1	Functionalization of Methane	464
13.1.1	Methane to Methanol/Formaldehyde	464
13.1.2	Dimerization of Methane	466
13.1.3	Aromatization of Methane	467
13.2	Functionalization of C ₂ –C ₄ Alkanes	468
13.2.1	Oxidation of C ₂ –C ₄ Alkanes	468
13.2.2	Dehydrogenation of C ₂ –C ₄ Alkanes	470
13.2.3	Aromatization of C ₂ –C ₄ Alkanes	471
13.3	Carbon Black	472
	Endnotes	473
14.	Chemicals from Coal	475
14.1	Chemicals from Coke Oven Distillate	477
14.2	The Fischer–Tropsch Reaction	480
14.3	Coal Hydrogenation	484
14.4	Substitute Natural Gas	485
14.5	SNG and Synthesis Gas Technology	485
14.6	Underground Coal Gasification	488
14.7	Calcium Carbide	488
14.7.1	The Chinese Chemicals to Coal Program	489
14.8	Coal and the Environment	490
	Endnotes	491
15.	Fats and Oils	493
15.1	Markets for Fats and Oils	495
15.2	Purification of Fats and Oils	497
15.3	Fatty Acids	499
15.3.1	Applications of Fatty Acids	501
15.4	Fatty Nitrogen Compounds	502
15.5	“Dimer” Acid	504

15.6	Aminoamides and Imidazolines	506
15.7	Azelaic, Pelargonic, and Petroselinic Acids	507
15.8	Fatty Alcohols	508
15.9	Epoxidized Oils	509
15.10	Ricinoleic Acid	510
15.11	Glycerol	512
15.11.1	Established Glycerol Uses	512
15.12	Alcoholysis of Fats and Oils	513
15.12.1	Cocoa Butter and Mothers' Milk	513
15.12.1.1	Mothers' Milk	515
15.12.2	Trans Fats and Interesterification	515
15.12.3	Biodiesel and Lubricants	516
15.12.3.1	Algae	518
15.13	Alkyl Polyglycosides	519
15.14	Non-Caloric Fat-like Substances	519
	Endnotes	520
16.	Carbohydrates	523
16.1	Sugars and Sorbitol	523
16.1.1	Isosorbide	530
16.2	Furfural	530
16.3	Starch	532
16.4	Cellulose	535
16.4.1	Miscellaneous Chemicals from Wood	539
16.4.1.1	Vanillin	541
16.4.1.2	Levulinic Acid	542
16.5	Gums	543
16.6	Fermentation and Biotechnology	544
16.6.1	Amino Acids	547
16.6.1.1	L-Glutamic Acid	547
16.6.1.2	L-Lysine	547
16.6.1.3	L-Aspartic Acid	548
16.6.1.4	L-Cysteine	549
16.6.2	Polymers	550

16.6.3	Proteins by Recombinant DNA Technology	550
16.6.4	Fermentation and Renewables Scenarios	551
16.6.5	Biofuels	554
16.6.5.1	The Brazilian Experience	554
16.6.5.2	Is U.S. Bioethanol a Renewable Energy Source?	555
16.6.5.3	Biomass as Feedstock	556
16.6.5.4	Catalytic Bioforming	556
16.6.5.5	Biotechnology Versus Synthesis Gas	557
	Endnotes	558
17.	How Polymers Are Made	561
17.1	Polymerization	565
17.2	Functionality	568
17.3	Step Growth and Chain Growth Polymerizations	571
17.3.1	Free Radical Polymerization	573
17.3.2	Chain Transfer	575
17.3.3	Copolymerization	577
17.3.4	Molecular Weight	579
17.3.5	Polymerization Procedures	580
17.3.5.1	Photoinitiation	582
17.3.6	Ionic Polymerization	584
17.3.7	Living Polymers	589
17.3.8	Block Copolymers	589
17.3.9	Graft Copolymers	592
17.3.10	Metal Complex Catalysts	593
17.3.11	Metal Oxide Catalysts	598
17.3.12	Metallocene and Other Single Site Catalysts	599
17.3.12.1	Single Site Nonmetallocene Catalysts	602
17.3.12.2	Late Transition Metal Catalysts	603
17.3.12.3	Commercial Prospects of LLDPEs	604
17.4	Examples of Step Polymerization	605
17.4.1	Phenoplasts and Aminoplasts	605
17.4.2	Polyurethanes	606
17.4.3	Epoxy Resins	611
17.4.4	Dendritic and Hyperbranched Polymers	613
17.4.5	Conducting Polymers	617
17.4.6	Conducting and Semiconducting Inks	621

17.5	Polymer Properties	622
17.5.1	Crystallinity	622
17.5.2	Glass Transition Temperature, Crystalline Melting Point, and Softening Temperature	626
17.5.3	Molecular Cohesion	628
17.5.4	Stress–Strain Diagrams	628
17.6	Classes of Polymers	630
17.7	Plastics Fabrication Techniques	631
	Endnotes	635
18.	Industrial Catalysis	637
18.1	Catalyst Choice	637
18.1.1	Reaction Velocity and Selectivity	638
18.1.2	Recovery of Unchanged Catalyst	641
18.1.3	Catalyst Deactivation	642
18.1.4	Access to Nonequilibrium Products	642
18.2	Homogeneous and Heterogeneous Catalysis	643
18.2.1	Reactors for Heterogeneous Catalysts	644
18.2.2	Immobilization of Homogeneous Catalysts	646
18.3	Catalyst Markets	647
18.4	Catalysis by Acids and Bases	651
18.5	Dual Function Catalysis	654
18.6	Catalysis by Metals, Semiconductors, and Insulators	655
18.6.1	Catalysts for Automobile Emission Control	656
18.7	Coordination Catalysis	657
18.7.1	Catalysts for Stereoregular Compounds	658
18.7.2	Asymmetric Synthesis	660
18.8	Enzymes	661
18.8.1	Catalytic Antibodies	663
18.9	Shape-Selective Catalysts	664
18.10	Phase-Transfer and Fluorous Biphase Catalysis	669
18.11	Nanocatalysis	670
18.12	Catalysts of the Future	673
18.12.1	Catalyst Design	673
18.12.2	Higher Selectivities	673

18.12.3	Catalysts with Greater Activity	674
18.12.4	Pollution Problems	675
18.12.5	Catalysts for New Reactions	675
18.12.6	Catalysts that Mimic Natural Catalysts	676
18.12.7	Catalyst Discovery Via High Throughput Experimentation	676
	Endnotes	677
19.	Green Chemistry	681
19.1	The Decline of Acetylene Chemistry	683
19.2	Nylon	683
19.3	Replacement of Phosgene	684
19.4	Monomethylation by Dimethyl Carbonate	685
19.5	Liquid and Supercritical Carbon Dioxide and Water	685
19.6	Ionic Liquids	687
19.7	Photocatalysts	690
19.8	Paired Electrosynthesis	691
19.9	“Green” Pharmaceuticals	692
19.9.1	Ibuprofen	692
19.9.2	Sertraline	694
19.9.3	Pharmaceuticals from “Renewables”	696
19.10	Catalytic Dehydrogenation of Diethanolamine	698
19.11	Genetic Manipulation	698
19.12	Biodegradable Packaging	698
19.12.1	Polyhydroxyalkanoates	701
19.13	The Presidential Green Chemistry Challenge Program	703
	Endnotes	704
20.	Sustainability	707
20.1	Climate Change	708
20.2	Resource Depletion	712
20.2.1	Food, Water, and People	713
20.2.1.1	Food	713
20.2.1.2	Water	714
20.2.1.3	People	715

20.3	Energy Sources	717
20.3.1	Wind Power	719
20.3.2	Wave Power	720
20.3.3	Solar Power	721
20.3.3.1	Concentrated Solar Power	721
20.3.3.2	Photovoltaic Cells	721
20.3.3.3	Dye-Sensitized Solar Cells	722
20.3.3.4	Artificial Photosynthesis	724
20.3.4	Nuclear Energy	726
20.3.5	Methane Hydrate	727
20.3.6	The Hydrogen Economy	728
20.3.7	Fuel Cells	729
20.3.8	Electric Vehicles	735
20.4	Pollution	736
20.4.1	The Ozone Layer	738
20.4.2	Trace Chemicals	742
20.4.2.1	Pesticides	742
20.4.2.2	Nonpesticide Lipophiles	743
20.4.3	Air Pollution	744
20.4.3.1	Sulfur Dioxide Particulates	745
20.4.3.2	Automobile Exhaust Emissions	748
20.4.4	Water Treatment	750
20.4.5	Solid Wastes	752
20.4.5.1	Waste Prevention	753
20.4.5.2	Recycling	754
20.4.5.3	Combustion/Incineration	755
20.4.5.4	Sanitary Landfill	756
20.4.6	Petrochemical Industry Wastes	758
20.4.7	Other Environmental Problems	759
20.5	Valediction	759
	Endnotes	761
	Appendix A: A Note on Cost Calculations	765
	Appendix B: Units and Conversion Factors	771
	Appendix C: Special Units in the Chemical Industry	773
	Appendix D: The Importance of Shale Gas and Shale Oil	775
	Index	779

PREFACE

This third edition of *Industrial Organic Chemicals* is prompted by the impact of globalization and of threats to the environment. This is not to say that industrial chemistry has stood still – very much the reverse, and we have featured much new chemistry. All the same, our earlier books were about the exciting new world of petrochemical feedstocks and the ingenious new products that could be made from them. In this edition, the exciting new processes have become the dull traditional ones. Well-established processes of technology transfer have carried them to developing countries, especially those that produce petrochemical feedstocks. In addition, humankind's activities are seen both as depleting the resources of the planet and of polluting it to the point at which humankind will drown in its own effluvia. The extent of these threats is hotly contested; nonetheless, the chemical industry both contributes to the problems and is instrumental in trying to solve them.

There have been many developments since the second edition, and the following topics have gained especially in significance:

- The world chemical industry has migrated from the United States, Western Europe, and Japan to the Middle East and to Asia-Pacific, especially China. Will shale oil and gas bring it back? (See Appendix D).
- There is increased emphasis on environmental issues, with pressure on companies to clean up polluting processes or replace them with environmentally friendly ones.
- Globalization has changed patterns of transportation of chemicals with, for example, solid polymers rather than petrochemical feedstocks being shipped from the Middle East.
- The discovery of vast reserves of shale gas has altered the long-term predictions of resource depletion in the United States and other countries.
- Considerations of sustainability and the threat of climate change have prompted research into processes (including electricity generation) that produce less or no carbon dioxide, or come from renewable resources.

We have retained some material that is now largely of historical interest, partly for sentimental reasons, but partly because the three authors have watched the

meteoric rise of the chemical industry from its early days to its present-day maturity. We think there is a value in our readers observing how technology has developed, and the social, technological, and economic changes that have brought it to its present position.

HAROLD A. WITTCOFF

PREFACE TO THE FIRST EDITION

In the early 1970s, one of us (BGR) wrote a book celebrating the rapid growth of the adolescent chemical industry. The organic chemicals industry at the time was growing at four times the rate of the economy. It was indicated nonetheless that “trees do not grow to the sky.” In 1980, in another book, we both declared the industry to be middle-aged with slow or zero growth. In this totally revised and expanded version of our earlier book, we reflect that the industry, at any rate in the developed world, is showing many of the illnesses of late middle-age.

The problems have arisen first from the undisciplined building of excess capacity with consequent fierce competition and low prices. Second, the entry of numerous developing countries into the industry has exacerbated the situation (Section 1.3.6), and third, there has been much stricter government legislation (Section 1.3.7). There is massive worldwide restructuring and continual shifting of commodity chemical manufacturing to areas other than the United States, Western Europe, and Japan. The Middle East and Southeast Asia are the principal new players in the game. Perhaps this trend will continue and the present developed world will in the future confine itself to the manufacture of specialties, but the economic and political forces at work are more complex than that. We hope to be able to discuss their resolution in another edition in about 10 years’ time.

Meanwhile, some things have not changed. The organic chemicals industry is still based on seven basic raw materials all deriving from petroleum and natural gas. The wisdom of teaching about the chemical industry on the basis of these seven building blocks has been confirmed by the fact that, since the publication of our first book, one of us (HAW) has delivered by invitation 300 courses in 28 countries on the fundamentals of the industry based on this pattern. Most of these courses are for industrial personnel but academia has not been neglected.

Furthermore, some changes have been positive. For example, there have been exciting new processes such as the development of metallocene catalysts (Section 15.3.12). Section 4.6.1 describes new methyl methacrylate processes that give a potentially cheaper product, that do not produce ecologically undesirable ammonium hydrogen sulfate by-product or (in another process) that eliminate the use of dangerous hydrogen cyanide.

In this book, our main objective is still to present the technology of the organic chemicals industry as an organized body of knowledge, so that both the neophyte and the experienced practitioner can see the broad picture. Nonetheless, we have expanded its scope to include not only new processes but many apparently less

important reactions that are significant because they give rise to the more profitable specialty chemicals. The lesser volume chemicals have been clearly delineated as such and the reader who wishes to see the industry on the basis of its large tonnage products can omit these sections.

We hope this book will be useful both to college students who have studied organic chemistry and to graduates and industrial chemists who work in or are interested in the chemical industry. Even though much of the chemistry has remained the same, the change in the way the industry looks at its problems provides ample justification for our offering this edition as a fresh perspective on industrial organic chemicals.

PREFACE TO THE SECOND EDITION

In the preface to the first edition, we expressed the hope that we could comment on the chemical industry's evolution in 10 years' time. Dramatic changes have motivated us to compress this time frame. There have been unprecedented restructuring, severe and complicated feedstock problems, and massive shifts of capacity to developing countries, whose economic and political stability is in doubt. Possible terrorist activity dictates elaborate safety and security procedures and the design of plants with small inventories is a priority.

To increase our cover, particularly of the patent literature, we have invited Dr. Jeffrey S. Plotkin, Director of the Process Evaluation and Research Planning program at Nexant ChemSystems to join us as co-author.

ACKNOWLEDGMENTS

We are grateful to the many friends and colleagues with whom we spoke often during the revision of this book. Much knowledge and clarification evolved in this way. Nexant ChemSystems Inc.'s numerous multiclient reports provided detailed information on both reaction conditions and production economics.

We thank Prof. Maurice Kreevoy for his review of the catalyst chapter and his many helpful suggestions. We also thank librarians Mrs. Denise Phillips and Ms Lorraine Moneypenny who searched the literature diligently for us. Ms Pat Cairns cheerfully did many things to make the revision easier, and we thank her sincerely. We also thank Mr. Ted Wittcoff who good naturedly compensated for his father's computer shortcomings.

Bryan was one of the UK's first mass-spectrometrists and a pioneering teacher in industrial chemistry. His early love of chemistry was developed with experiments—many of them explosive—in his father's pharmacy. Bryan won a scholarship to the Queen's College, Oxford, to study chemistry. With his PhD he went onto a post-doctoral fellowship at Brookhaven National Laboratory in New York, where he worked with Lewis Friedman on the kinetics of gas-phase ion-molecule reactions. Bryan found living in the U.S. both exciting and stimulating and was always pleased to return there for work and for holidays.

Bryan returned to the UK to work for Distillers as a physical chemist but after only a year moved to sales development. This led to a career determining lifelong interest in the relationship between chemistry and economics. In 1963 he moved from commerce to academia at Battersea College of Advanced Technology (soon to become the University of Surrey) where he first met his great friend Michael L. Burstall. Together they developed a ground breaking industrial chemistry course and wrote one of the standard works in the field, *The Chemical Economy* (1973). In 1977 Bryan moved to the chemical engineering department of Borough Polytechnic (later London South Bank University) as principal lecturer responsible for organizing and developing research. He was appointed Professor of Chemical Technology in 1990.

Bryan was a teacher with a gift for explaining complex problems with clarity and wit, which is probably why he had many invitations to work abroad. In 1972 he spent a sabbatical year at the Hebrew University, Jerusalem, where he helped to set up the Master's program in applied chemistry and lectured on industrial processes and catalysis. He later taught at the Weizmann Institute and at the universities of Bar Ilan and Ben Gurion and acted as a consultant for the Israel Ministry of Development. In 1979 he taught at the Universities of Texas, Oregon, Michigan, and Missouri and in 1981 was visiting professor and consultant at the University of Campinas, Brazil.

Apart from his scientific work, Bryan had a life long interest in the arts. At Oxford he wrote comedy revues and sketches and at Brookhaven he directed the local amateur dramatic society in several revues and plays and also took to the stage as an actor, a hobby which he continued on his return to England. His journalism continued until 2012. He delighted in writing satirical articles and book reviews on a wide variety of subjects. However it was always his wish to write a book for the popular market ("such as people might buy at airports" as he used to say) and in 2008 he wrote *Bread—a Slice of History*, together with John Marchant and Joan Alcock, colleagues from South

Bank University. He enjoyed appearing as an authority on bread on the BBC4 program “In Search of the Perfect Loaf.”

Since his early twenties, Bryan had been an enthusiastic and expert skier. He delighted in taking his family and later also his grandchildren, on skiing holidays. He continued to do this until 2011, despite a catastrophic ski accident in 1987 in which he broke many bones and tore his aortic valve. In the preface to *Pharmaceutical Chemicals in Perspective*, which he wrote with Harold Wittcoff in 1988, Bryan thanked the doctors in Grenoble who had saved his life. He was also grateful to the pharmaceutical industry, whose drugs allowed him to survive for many more years and two further open heart operations.

Professionally, Bryan published more than 140 papers on the chemical, pharmaceutical and process industries, as well as 13 books, many of which became standard works, including *Industrial Organic Chemicals in Perspective* (1980) with Harold Wittcoff. Harold met Bryan after the publication of *The Chemical Economy* (1973). In the years to come, Bryan and Harold worked together on many projects and they became close friends as well as colleagues. Their collaboration was a source of great joy not only to Bryan but to his entire family. Bryan was planning to work on the proofs of this third edition of *Industrial Organic Chemicals* the week before he died. He would be delighted and proud to know that all their hard work has come to fruition.

LIST OF ACRONYMS AND ABBREVIATIONS

ABS	Acrylonitrile–butadiene–styrene
ACS	American Chemical Society
AFC	Alkali fuel cell
AMOCO	Formerly American Oil/Standard Oil of Indiana, now owned by BP
AO	Acid optimization
APPE	Association of Petrochemicals Producers in Europe
ARCO	Formerly Atlantic Richfield Oil Company, now owned by Lyondell
BASF	German chemical company: formerly Badische Anilin und Soda Fabrik
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BP	British Petroleum
BPA	Bisphenol A
Btu	British thermal units (see Appendix B)
BTX	Benzene–toluene–xylene
CAA	Clean Air Act
CEFIC	Centre Européen des Fédérations de L’Industrie Chimique
CFCs	Chlorofluorocarbons having no hydrogen atoms
CHP	Combined heat and power
CIA	UK Chemical Industries Association
CIS	Commonwealth of Independent States (formerly USSR)
CMA	Chemical Manufacturers’ Association
CMC	Carboxymethylcellulose
CMRs	Carcinogens, mutagens, and reprotoxins
CNI	Chemical News Intelligence
COCs	Cyclic olefin copolymers
CRG	Catalytic rich gas
DCC	Deep catalytic cracking
DDT	Bis(chlorophenyl)trichloromethylmethane
DEA	Diethanolamine
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSM	Dutch chemical company; formerly Dutch State Mines
EDTA	Ethylenediaminetetraacetic acid
ENI	Italian chemical company: Ente Nazionale Idrocarburi (Enichemi is a subsidiary)

EP	Ethylene–propylene (rubber)
EPA	Environmental Protection Agency
EPDM	Ethylene–propylene–diene monomer
EVA	Ethylene–vinyl acetate
EVC	European Vinyls Corporation
FCC	Fluid catalytic cracking
FDA	Food and Drug Administration
GATT	General Agreement on Trade and Tariffs
GLA	Gamma-linolenic acid
GMP	Good Manufacturing Practice
GTL	Gas to liquid
HTE	High throughput experimentation
HCFCs	Hydrochlorofluorocarbons
HCN	Hydrocyanic acid and hydrogen cyanide
HDPE	High density polyethylene
HIPS	High-impact polystyrene
HMDA	Hexamethylenediamine
HMDI	Hexamethylene diisocyanate
HMSO	Her Majesty’s Stationery Office
ICI	UK Chemical Company; formerly Imperial Chemical Industries
IFP	Institut Français de Pétrole
IPDI	Isophorone diisocyanate
IR	Infrared
ISP	International Specialty Products
IUPAC	International Union of Pure and Applied Chemistry
KA	Ketone/alcohol
LAB	Linear alkylbenzene
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LPG	Liquid petroleum gas
LVN	Light virgin naphtha
M/F	Melamine–formaldehyde
MBS	Methyl acrylate–butadiene–styrene
MCFC	Molten carbonate fuel cell
MDI	4,4'-Diphenylmethane diisocyanate
MEK	Methyl ethyl ketone; 2-butanone
MOI	Mobil olefin interconversion
MON	Motor octane number
MTBE	Methyl <i>tert</i> -butyl ether
MTG	Methanol to gasoline
MTO	Methanol to olefins
MTP	Methanol to propylene
NAICS	North American Industry Classification System
NPRA	National Petroleum Refiners Association
OSHA	Occupational Safety and Health Act

P/F	Phenol-formaldehyde
PAFC	Phosphoric acid fuel cell
PAMAM	Poly(amidoamine)
PAN	Peroxyacetyl nitrate
PBBs	Polybrominated biphenyls
PBDEs	Polybrominated diphenyl ethers
PBT	Persistent bioaccumulative toxic
PDJ	Patents and Design Journal
PEEK	Poly(ether ether ketone)
PEMFC	Polymer electrolyte–proton exchange membrane fuel cell
PEN	Poly(ethylene naphthalate)
PERP	Process evaluation and research planning
PET	Poly(ethylene terephthalate)
PIMM	Process integrated management methods
PMDA	Pyromellitic dianhydride
PO	Propylene oxide
POX	Noncatalytic partial oxidation
PTA	Pure terephthalic acid
PTFE	Polytetrafluoroethylene
PVC	Poly(vinyl chloride)
REACH	Registration, authorization, and evaluation of chemicals
RIM	Reaction injection molding
RIPP	Chinese Research Institute of Petroleum Processing
RON	Research octane number
SABIC	Saudi Arabia Basic Industries Corporation
SAN	Styrene–acrylonitrile
SAPO	Silicaaluminophosphate
SBR	Styrene–butadiene rubber
S-B-S	Styrene–butadiene–styrene
S-E-B-S	Styrene–ethylene–butylene–styrene
S-E-P-S	Styrene–ethylene–propylene–styrene
SHOP	Shell Higher Olefins Process
SI	Système International
S-I-S	Styrene–isoprene–styrene
SMDS	Shell Middle Distillate Synthesis
SNG	Substitute natural gas
SOFC	Solid oxide fuel cell
SOHIO	Was Standard Oil of Ohio; now part of BP
TAME	<i>tert</i> -Amyl methyl ether
TBA	<i>tert</i> -Butylbenzaldehyde
TDI	Toluene diisocyanate
THF	Tetrahydrofuran
TMA	Trimellitic anhydride
TNT	Trinitrotoluene
TPA	Terephthalic acid

xxxvi LIST OF ACRONYMS AND ABBREVIATIONS

U/F	Urea-formaldehyde
UOP	Universal Oil Products
USGC	United States Gulf Coast
USGS	United States Geological Survey
USSR	Union of Soviet Socialist Republics (Soviet Union) now CIS

INTRODUCTION

How to Use Industrial Organic Chemicals, Third Edition

This new edition is the latest in a series of books by the authors on the technology and economics of the chemical industry. It is justified by the rapid rate of change in the industry. We discuss many new processes and improvements in many older ones. There have also been extensive changes in the economics of the industry, in its location and in issues of “green” chemistry and sustainability.

This introductory chapter was originally intended to show, first, the origin of our information and, second, where you may follow up topics that arouse your interest. These aims have been retained, but we have revised our approach to information gathering to reflect the influence of the Internet. Indeed, for all we know, you are reading this on an e-book reader or have downloaded it onto your mainframe.

The answer to the question “Where did we get our information from?” is “We sort of picked it up in fifty years or so associated with the industry.” A 2010 book on a topic related to ours has run to several editions. Its general bibliography contains 20 books of which 13 were published before 1980. These sources are long out of print and inaccessible to the general reader. This has prompted us to delete all references before 1990 and most before 2000, apart from a few books and articles of emotional or historical significance. Readers interested in the earlier bibliographies should consult our earlier editions. Much of our information also accrued during courses on the chemical industry given over many years by the authors, most recently under the auspices of Nexant/ChemSystems. One author (HAW) has presented this course in 28 countries (many several times) to over 1000 students and we have drawn on information and illustrations from it.

The answer to how you follow up your interests today is also different. Two generations ago, the conscientious worker would read the professional journals, sift through the learned journals, and check with Chemical Abstracts or one of its

associated services. On an occasional visit to a large library, he or she would browse the open shelves around a Dewey decimal number of interest and see what new books there were. Business information was like gold dust. Marketing people hung around bars that employees of rival companies frequented and tried to piece together what was actually happening from the fragments of information that were dropped.

Today, one types keywords into Google and gets, at a conservative estimate, a million hits. We have passed from information famine to information overload. The problem is to sort the correct information from the speculative and the mistaken. The press has reported indignantly that Google keeps records of one's previous searches and places items it thinks will be of interest high on its listings. That seems a blessing rather than a curse. The drawback of citing URLs (internet addresses, known as Uniform Resource Locators) is that some of them disappear with time, and also that the URL copied from one's browser is sometimes accessible only through the home page of the organization producing the information. We recommend readers who get error messages when following our URL citations to try to address the home page of the organization concerned and to navigate from there.

Wikipedia is a treasure house of information and is much more reliable on scientific than on political matters. It is the starting point for many searches and provides references to more detailed sources. We have cited it unashamedly. Furthermore, we have reduced direct references to the scientific literature and have preferred to cite URLs, chemical industry journals, and professional magazines. These report novel developments and provide threads that lead to the more solid literature. We are not sure how user-friendly this will turn out to be, but we feel that it is at least some sort of response to changes in the way people search for information.

1.1 WHY THIS BOOK WAS WRITTEN AND HOW IT IS STRUCTURED

The petrochemical industry provides well over 90% by tonnage of all organic chemicals. It grew rapidly in the 1950s and 1960s. Many new processes and products were introduced. Large economies of scale proved possible. The prices of chemicals and polymers dropped so that they could compete with traditional materials. Cheerfully colored plastic housewares, highly functional packaging, shampoos that tolerated hard water, and easy care garments of synthetic fibers were no longer exciting new technology but had become an accepted and routine part of modern life.

By the 1970s growth was leveling off. The first and second oil shocks increased the price of crude oil and hence of its downstream products. Economies of scale suffered a hiatus to rise again in the late 1990s with the construction of 1 million metric tons of ethylene per year steam crackers and 1.6 million metric tons per year methanol plants. The industry had matured. As its technology became better known and more available, developing countries started their own petrochemical industries, competing with the developed countries and thus depressing profitability. In the early 2000s the trickle of the industry to the Middle East and Asia-Pacific became a flood. For many products today, production in Asia-Pacific is greater than the United States and

Western Europe combined. The industry in the West has rationalized. Of the world's twenty leading chemical companies in 1990, only eight were flourishing in 2008.

Furthermore, the impact of the industry on the environment has become evident, and it stands accused of everything from promoting global warming to changing the sex of fish. While many in the industry think that much of this is motivated by anti-industry hype, there is still an important and widespread movement toward "greener" chemistry.

New products are no longer the name of the game partly because expensive toxicity testing is required before a new compound can be introduced. Thus, rather than developing bigger, better plants to manufacture novel chemicals, the industry is concerned with lessening pollution, improving processes, and developing specialty chemical formulations and niche products that can be sold at higher profit margins. Research and development has become highly process-oriented, in part to find less polluting processes, and in part to combat maturity and to gain an edge over competition with money-saving technology. Examples are given throughout the book.

Chapter 1 deals with the characteristics of the chemical industry and its place in the U.S. economy.

Chapter 2 deals with globalization – the spread of the chemical industry from the places it originated, namely, Western Europe and the United States, to Asia-Pacific and the Middle East.

Chapter 3 concerns the movement of chemicals from wherever they are produced – often from countries that had no chemical industry a generation ago – to wherever they are consumed. Transport is crucial in a globalized world and accounts for perhaps 10% of the cost of the average chemical.

Chapter 4 describes where organic chemicals come from and then shows how the major sources, petroleum and natural gas, provide seven basic chemicals or chemical groups from which most petrochemicals are made. The basic building blocks comprise olefins – ethylene, propylene, and the C₄ olefins (butadiene, isobutene, 1- and 2-butenes) – plus the aromatics, benzene, toluene, and the xylenes (*ortho*, *meta*, *para*) – and one alkane, methane. The chapter explains how the olefins derive primarily from steam cracking and secondarily from catalytic cracking, and how the aromatics derive primarily from catalytic reforming in the United States but from steam cracking in Europe. Methane occurs as such in natural gas, and reserves of this have recently been augmented by the supplies from abundant shale. The important interface between the refinery and the petrochemical industry is described as is the relationship between feedstock flexibility and profitability.

Chapters 5 and 6 describe the chemistry of ethylene and propylene. They are the most important of the seven building blocks and are treated accordingly.

Chapters 7 and 8 deal with the C₄ and C₅ olefins. The C₅ compounds and their derivatives are only used in low volume and are not included in the seven basic building blocks. They are nonetheless an important source of isoprene for a synthetic analog of natural rubber (Section 17.3.10) and for thermoplastic elastomers (Section 17.3.8).

Chapters 9, 10, and 11 describe the chemistry of the aromatics – benzene, toluene, and the xylenes. Benzene has been overshadowed by ethylene and propylene since the 1960s but is still the third most important of the building blocks.

Chapter 12 describes the chemistry of methane, a relatively unreactive molecule, which nonetheless is the source of synthesis gas ($\text{CO} + \text{H}_2$) for ammonia and methanol manufacture. “Stranded” natural gas is a methane source that needs to be exploited. Acetylene is discussed here, since it may be made from methane. Very important fifty years ago, its significance has been steadily decreased by newer chemistry based on ethylene and propylene, but it has recently made a comeback in the fast-developing Chinese chemical industry with its strong emphasis on coal.

Chapter 13 is devoted to the growing industrial chemistry based on alkanes other than methane. The substitution of alkanes for olefins, which depends on sophisticated catalyst development, could change industrial chemistry profoundly in the future.

Chapters 14, 15, and 16 deal with nonpetroleum sources of chemicals – coal, fats and oils, and carbohydrates. The chemical industry in the nineteenth and early twentieth centuries was based on chemicals derived from coal tar or coke oven distillate. Today, this is a specialty area, and our major interest in coal focuses on its conversion to synthesis gas. This would be the first stage in building a coal-based chemical industry should petroleum and natural gas become depleted, and it is already being revived in China.

The chemistry of fats and oils (Chapter 15) is reflected in the surfactant area and in numerous specialty performance products. Carbohydrate-based chemicals (Chapter 16) are also largely specialties. These two groups are nonetheless sources of renewable raw materials and their conversion often employs biotechnology. As these materials are primarily agricultural products, their use competes with foodstuffs production and is attracting not only research interest but also debate as to its wisdom.

Since the overwhelming majority of all organic chemicals manufactured end up in polymers, Chapter 17 is devoted to polymerization processes and polymer properties. Recent developments in metallocene catalysts, dendrimers, and conducting polymers are included. Chapter 18 deals with the all-important subject of catalysis without which there would hardly be a chemical industry. Chapter 19 deals with the emergence of “green” chemistry, a topic that dominates the books published on industrial chemistry since 1990. Finally, Chapter 20 deals with the vital issue of sustainability, both in terms of individual problems (air pollution, waste disposal, electricity from solar cells, etc.) and global issues such as international competition and resource depletion.

It is the new processes and attitudes that provided the incentives for this third edition, but we have also expanded its scope to include many apparently less important reactions, which are significant because they give rise to the more profitable specialty chemicals. We have also retained details of some obsolete processes, not only because they may one day be revived, but also because it is crucial to understand why one process might supplant another.

We hope this book will be useful both to university students who have studied organic chemistry, and to graduates, industrial chemists, and managers who work in or are interested in one of the most remarkable industries of the twentieth century and, even though we have only experienced a decade of it, the twenty-first century.

We intend each chapter to be self-sufficient; hence there is inevitably a degree of repetition. We have tried to minimize this by extensive cross-referencing and hope the reader will be tolerant of what remains.

I.2 NORTH AMERICAN INDUSTRY CLASSIFICATION SYSTEM

The U.S. government provides statistics on all branches of industry, dividing them according to the North American Industry Classification system (NAICS) ([http://www.census.gov/cgi-bin/sssd/naics/naicsrch?chart_code=31&search=2007 NAICS Search](http://www.census.gov/cgi-bin/sssd/naics/naicsrch?chart_code=31&search=2007%20NAICS%20Search)). The 2002 revisions were further revised in 2007. Each major segment of the economy is classified under a number between 1 and 99 (see Table 1.1). Manufacturing industries are classified under numbers 31–33 and the chemical and allied products industry falls within this category at 325. Statistics for subsegments of the industry are provided under four-, five-, or six-digit numbers. Thus 3252 is *Resins, synthetic rubbers & artificial & synthetic fibers and filaments*, 325211 is *Plastics materials and resins*, 325212 is *Synthetic rubber*, and 32522 is *Artificial & synthetic fibers and filaments*. We have relied on these data for our book, although it is never possible to obtain up-to-date figures. Thus the material published in 2010 contains information for 2008. The more detailed figures from the 2010 census are appearing piecemeal. Statistics from other sources are often more up-to-date but are less authoritative (Section I.4.5).

The industries that form the chemical and allied products industries are shown in Table 1.2. Although at times one might wish for even more detailed information, the North American Industry Classification provides a wealth of it. Other countries do not have comparable databases; many have Standard Industrial Classifications, but none is so detailed. The classifications in other countries rarely correspond to those in the United States or to each other, and analysts wishing to tackle official statistics should be aware of the pitfalls.

I.3 UNITS AND NOMENCLATURE

The widespread adoption of the SI (*Système international d'unités*) system of units based on the meter, the kilogram, and the second has worsened rather than improved the plethora of units used in the chemical industry. Three kinds of tons are in common use – the short ton (2000 lb), the metric ton or tonne (1000 kg or 2204.5 lb), and the long ton (2240 lb). U.S. statistics are frequently given in millions of pounds, which are at least unambiguous, but we give most of our figures in metric tons. In addition, we try to quote figures in the units actually used by industry – petroleum is measured in barrels, benzene in gallons, mixed xylenes in gallons, and (incredibly) *p*-xylene in pounds – and to give conversions into better known units. A table of conversion factors is given in Appendixes B and C.

Similarly, in naming chemicals, we tend to use the names conventional in industry rather than the more academic nomenclature of the International Union of Pure and

Applied Chemistry (IUPAC). Thus we write hydrogen not dihydrogen; ethylene, acetylene, and acetic acid; not ethene, ethyne, and ethanoic acid.

Industry makes no effort to use consistent nomenclature. Ethene and propene are universally known as ethylene and propylene and would scarcely be recognized by their IUPAC names. The C_4 olefins, however, are frequently referred to as butenes rather than butylenes, and we have followed this style. We use trivial names where industry does. Thus we refer to $C_6H_5CH(CH_3)_2$ as cumene, the name by which it is bought and sold, rather than the more informative names of isopropylbenzene, 2-phenylpropane, or (1-methylethyl)benzene. The term ethanal would be likely to be misread or misheard in industry as ethanol, and the compound is known as acetaldehyde. So important is trivial nomenclature that the pharmaceutical industry could not exist without it.

We regret the lack of consistency that the use of trivial nomenclature entails, but we feel it best serves our aim of communicating with chemical industry personnel and preparing students to enter the industry.

I.4 GENERAL BIBLIOGRAPHY

As noted above, we have “cleaned up” our bibliography to reflect the influence of the Internet. A rapid search of the Amazon website will provide lists of books on any conceivable topic. We assume that readers have access to background articles on most topics and we have provided endnotes to each chapter that replace the “notes and references” in earlier editions. These refer specifically to the information to which they are attached, even where anecdotal material is appended.

I.4.1 Encyclopedias

The most important single reference work is R. E. Kirk and D. F. Othmer, *Kirk–Othmer’s Encyclopedia of Chemical Technology*, Volumes 1–27, 5th ed., J. I. Kroschwitz and M. Howe-Grant, editors, Hoboken NJ: Wiley-Interscience; 2004–2007. *Kirk–Othmer* provides comprehensive and well-referenced coverage of almost every aspect of industrial chemistry. There is access to registered users (via a university or other subscriber) at www.mrw.interscience.wiley.com/uric or www.mrw.interscience.wiley.com/kirk, and these sites will also search the whole of the Wiley-Interscience collection. The earlier volumes of the first to fourth editions are inevitably dated but provide information not readily available from other sources. If a subject is not treated in the new edition, it is always worth consulting the older one.

The only encyclopedia to rival *Kirk–Othmer* is *Ullmann’s Encyclopedia of Industrial Chemistry*, M. Bohnett and F. Ullmann editors, Weinheim: Wiley-VCH. It was first published in 1914 and this, the sixth edition, appeared as a 40-volume set in 2003. It has a more international approach than *Kirk–Othmer* and is available online to subscribers.

The Encyclopedia of Polymer Science and Engineering, 3rd ed., J. I. Kroschwitz, editor (12 volumes plus supplement and an index volume), Interscience, New York: 2003-2004, provides comprehensive coverage of polymer chemistry.

The Encyclopedia of Chemical Processing and Design, J. J. McKetta and R. G. Anthony, editors, New York: Dekker; has a chemical engineering orientation. It had run to 69 volumes by 2002 but the publication process seems to have run out of steam. As it started in 1976, it is perhaps inevitable that the approach is inconsistent. Individual articles are worthwhile but the content is unpredictable.

R. D. Ashford, *Dictionary of Industrial Chemicals*, 2nd ed., London: Wavelength; 2002, and A. Comyns, *Encyclopedic Dictionary of Named Processes in Chemical Technology*, Boca Raton, FL: CRC Press; 3rd ed., 2007 are useful reference works.

Some consulting companies publish reports on a continuing basis that contain a wealth of up-to-date information on chemistry, engineering, and markets of numerous industrial chemicals. These are quite expensive, however, and are usually found only in industrial libraries, the subscriber agreeing to keep the information confidential. One such program is entitled *Process Evaluation and Research Planning (PERP Program)* Nexant Inc./ChemSystems, 44 South Broadway, White Plains, NY 10601-4425 USA, which covers in depth the chemistry, engineering, and market data for many of the basic petrochemicals as well as important specialty chemicals. We used to have great respect for the *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, CA, but since it was taken over by IHS (Information Handling Services) we confess we have not seen a copy. It is available by annual subscription or individual report.

1.4.2 Books

Before the spectacular growth of the chemical industry after World War II, three classic books appeared that encompassed much of what was done at that time. These books have been repeatedly revised and updated and, although they seem old-fashioned in some ways, they are certainly worthy of mention. The oldest and also, because it has been updated, the newest is, J. A. Kent and E. R. Riegel, *Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology*, 11th ed., New York: Springer; 2007. Riegel first appeared in 1928 as *Riegel's Handbook of Industrial Chemistry* and is now a multi-author survey of the chemical and allied products industry.

Chemicals are discussed from the point of view of the consumer in an interesting and original book, B. Selinger, *Chemistry in the Market-Place*, 5th ed., Sydney: Harcourt Brace; 1998. Selinger is a pioneer of the Australian consumer movement and chaired a committee on toxic waste disposal. He describes the formulation of many domestic products together with the reasons for the various additives and the theory behind them.

P. J. Chenier, *Survey of Industrial Chemistry*, 3rd ed., New York: Kluwer Academic-Plenum; 2002, contains well-written thumbnail sketches of about a hundred industrial organic chemicals plus a few inorganics. It describes some economic aspects of the industry but is strongly United States oriented. *Handbook of Petrochemicals*

Production Processes, R. A. Meyers, editor, New York: McGraw Hill; 2005, is described as a handbook, but is more a multi-author encyclopedic description of 53 industrial process technologies for producing 18 different petrochemicals.

S. Matar and L. F. Hatch, *Chemistry of Petrochemical Processes*, Boston: Gulf Professional Publishing, 2nd ed., 2001, is a competent exposition of petrochemistry, weak on social and economic implications but redeemed by excellent flow diagrams. Regrettably the second edition is changed only slightly from the first. Some will prefer R. A. Meyers, *Handbook of Petroleum Refining Processes*, 3rd ed., New York: McGraw Hill; 2003.

The University of York (UK) Chemical Education Centre publishes regular editions of D. Waddington et al., *The Essential Chemical Industry*, 5th ed. 2010. Each chapter deals effectively with a different chemical.

On the historical side, P. Spitz, *Petrochemicals: The Rise of an Industry*, New York: Wiley; 1988, contains fascinating detail of the early petrochemicals industry. P. J. T. Morris, editor, has compiled *From Classical to Modern Chemistry: The Instrumental Revolution*, Royal Society of Chemistry, London, 2002, which deals with the impact that advances in instrumentation, especially in environmental analysis and process control, have made on what chemists and chemical engineers do and how they think about their subject. The UK Chemical Industries Association has produced *Development of the UK Chemical Industry: A Historical Review*, CIA, London, 2000. Tony Travis et al. have recently published in paperback *Determinants in the Evolution of the European Chemical Industry, 1900–1939: New Technologies, Political Frameworks, Markets and Companies*, Heidelberg: Springer; 2010.

1.4.3 Journals

A serious student of the chemical industry must follow the trade press whose range of interests includes new products and processes, changes in the structure and prospects of the industry, takeovers and trades, mergers and demergers, as well as economic trends.

A selection of news magazines for English-speaking readers includes *Chemical and Engineering News* (weekly, ACS, Washington DC); *Hydrocarbon Processing* (monthly, Gulf Publishing, Houston, TX), *Chemistry and Industry* (fortnightly, Society of Chemical Industry, London), and *Chemistry World* (Royal Society of Chemistry, London). *European Chemical News* has died but its daughter publication, *Asian Chemical News* (Reed Business Information, UK), started in 1994 and appears to be thriving. IHS (Information Handling Services) has acquired two important journals, *Chemical Week* (weekly, IHS Inc., 140 East 45th Street, 40th Floor, New York, NY 10017; 133 Houndsditch, London EC3A 7BX) and *ICIS Chemical Business*, which formerly was *Chemical Market Reporter*. This last carried a comprehensive list of U.S. prices of almost all widely sold chemicals, but the last list appeared in 2006. Present prices can be obtained from *Chemical Week* by subscription. For those who are financially challenged, there is an ICIS weekly newsletter that can be e-mailed free, and this can be strongly recommended.

1.4.4 Patents

Patents are a device whereby the government grants inventors the sole right to exploit their inventions for a period of 20 years in the United States and the European Community, and similar periods in other countries. In return, the inventors disclose details of their inventions in their patent specifications. Recent legislation in the United States has extended the life of a pharmaceutical patent to 22 years under certain circumstances and similar patent term restoration has been enacted in Europe.

Patents lie at the heart of a developed society. It is difficult to see how innovation could take place if innovators were not rewarded for their efforts. “I knew that a country without a patent office . . . was just a crab,” said Mark Twain, “and couldn’t travel any way but sideways or backwards.” Meanwhile, the patent literature has grown exponentially. In the United States, it took about 200 years to amass four million patents, the four millionth having been issued in 1976. It took only 15 years to accumulate one million more patents, and U.S. Patent 5,000,000 was issued on 19 March 1991 to L. O. Ingram et al. It described the use of modern biotechnology to produce one of the oldest synthetic organic chemicals – ethanol. Patent 7,000,000 was issued in 2006, and by 17 May 2011 the number had reached 7,950,000.

Patent specifications are a major source of technical information. They often disclose information at a much earlier date than the scientific literature; sometimes they are the only source of such information. Negative results often appear in patents but not in scientific journals, and knowledge of what has been tried without success may save the working scientist much time.

Academic scientists shun patents because the introductions and claims are written in legal jargon with long convoluted sentences. Librarians shun them because they are published as individual items and are difficult to collect and bind. They have, however, one overwhelming advantage. They are classified by subject and can be subscribed to in this way, a copy of a U.S. patent costing \$3.00.

Patent applications are numbered consecutively as they are received by the U.S. Patent Office (U.S. serial number) and, when the patent is granted, it is assigned another number (U.S. patent number). Other patent offices do the same.

Brief accounts of patents appear in the chemical trade literature. *Chemical Abstracts* publishes a numerical patent index that lists each patent number together with its corresponding Chemical Abstracts abstract number, country of origin, and serial number. It also provides a worldwide list of major patent offices and their addresses. *Chemisches Zentralblatt* (Akademie Verlag, Berlin) offers a similar service together with a guide to its use (*Chemisches Zentralblatt: das System*). Derwent (Thomson/Derwent, 14 Great Queen Street, London WC2 5DF, UK) publishes analyses and abridgements of patents from every country classified by subject, and provides monthly bulletins, for example, *Organic Patents Bulletin* and *Pharmaceutical Patents Bulletin*. Derwent has contributed greatly to making patent literature available.

The *Official Gazette*, copies of patents, coupon books (a convenient way to pay for copies), listings of patents by subject, copies of foreign patents, and much other

information may be obtained from the Commissioner of Patents and Trademarks, Washington DC 20231. Although many official and commercial organizations exist to help the student of the patent literature, a thorough search can be conducted only at the National Patent Library, Washington DC.

In the United Kingdom, the equivalent of the *Official Gazette* is the *Patents and Design Journal (PDJ)*, and it and other information are available from the Patent Office, Concept House, Cardiff Road, Newport, NP10 8QQ. The departure of the Office from London has been compensated for by a Central Inquiry Unit, telephone 0845 9500505, website www.patent.gov.uk. A thorough search can be carried out at the British Library (Patents Section), 96 Euston Road, London NW1 2DB.

Information on subject codes and many other aids to patent searching may be found in *Kirk-Othmer* (Section I.4.1). Highly praised for its clarity and sound advice is *The Business of Invention*, P. Bissel and G. Barker, Wordbase, Halifax, West Yorkshire, UK.

Access to patents has been simplified greatly by computerized searching of patent databases of which Derwent, *Chemical Abstracts*, *Inpadoc*, and *esp@cenet* are the most important. The United States (www.uspto.gov), European (www.european-patent-office.org/inpadoc), and British Patent Offices (gb.espacenet.com) are all online. Delphion Research, founded in 2000, has established an intellectual property network that can be subscribed to at a variety of levels ranging from full premier membership to a one-day pass. It enables one to perform text searches of United States, European, and Japanese patents, plus other intellectual property resources. Searching can be done by patent number or subject. WIPO, the World Intellectual Property Organization, based in Geneva, produces many CD-ROM and online publications dealing with the state-of-play of patents throughout the world. This has become more important as more countries have come into line with the GATT (General Agreement of Trade and Tariffs) regulations.

Although use of these databases requires skill, the user is rewarded by the access these bases provide to vast amounts of information. It is said that the Japanese have been able to accomplish a great deal in the chemical industry because of their skill in reading and interpreting patents. As the industry becomes more and more competitive, it is important to monitor trends, to know what other companies are doing, and to avoid duplication. The patent literature can contribute more than any other source to “knowing what your neighbor is doing,” an important concept in today’s technical world where an inventor can bring a new frame of reference to someone else’s invention to create new and unanticipated goods and services.

I.4.5 Statistics and Internet Sources of Information

Students of the commercial side of the chemical industry will require access to statistics of production and consumption. We have given sample statistics in this new edition but have been hindered by the fact that most of the revision was performed before the appearance of data for 2010. However, 2009 was a year of recession, so that the use of 2009 figures gives a misleading impression. In general, therefore, we have used 2008 as a base year, although we have updated in various areas.

Comprehensive U.S. statistics were formerly published annually by the United States International Trade Commission as *Synthetic Organic Chemicals: United States Production and Sales*. Publication ceased after 1994 on the spurious grounds that the data were available from other sources. The National Petroleum Refiners' Association (NPRA) took over some of the operation and makes the information, mainly on petrochemicals, available to member companies.

Various publications appear annually. The Chemical Manufacturers Association produces the handbook. It contains general information about the chemical industry including sales, volumes, pollution and environmental problems, and trends. The U.S. Business and Defense Services Administration publishes the *Chemical Statistics Directory* and the United States Office of Domestic Commerce, Chemical and Drugs Section, publishes its *Industry Report*.

The American Chemical Society has a website, www.chemistry.org, that gives links to sources of industrial data, usually, let it be said, to the relevant issues of *Chemical & Engineering News* (see below), which is an ACS publication.

Figures for the major chemicals plus much information about companies, employment, and related topics are published more rapidly in *Chemical & Engineering News* at the end of June or the beginning of July of the subsequent year. Thus the data for 2009 were published in the 5 July 2010 edition. An important major source is the *Guide to the Business of Chemistry*, American Chemistry Council, 1300 Wilson Blvd., Arlington, VA 22209. The United States Bureau of the Census (www.census.gov/compendia/statab/) has statistics for the NAICS group 325 and its subgroups (see Section I.2) at http://factfinder.census.gov/servlet/IBQTable?_bm=y&-_skip=300&-ds_name=AM0831GS101&-_lang=en. The results of the more detailed 2010 census should be available soon. The Statistical Abstract of the United States is produced by the U.S. Census Bureau and has heavily aggregated data about chemicals.

Publications by the United Nations and the UK Chemicals Industry Association are fairly light on statistics, but detailed figures may be obtained rather belatedly from government sources in most countries. In the United Kingdom, disaggregated figures appear relatively quickly in the *Business Monitor*, HMSO, London, and are summarized in, for example, *Business Monitor, Report on the Census of Production*, summary volumes published occasionally, HMSO, London.

In Europe, too, many useful data and some comments are published by the industry association CEFIC (Centre Européen des Fédérations de L'industrie Chimique) and by their subsidiary APPE, the Association of Petrochemicals Producers in Europe, who produce an annual *Activity Review* of exceptional interest. CEFIC material is most easily available online at www.cefic.org and www.petrochemistry.net. They have as members a range of associations dealing with lower olefins, aromatics, acetyls, acrylonitrile, amines, ethanol, acrylic monomers, plasticizers and intermediates, fuel oxygenates, ethylene oxide and derivatives, methanol, phenol, propylene oxide and glycols, oxygenated solvents, hydrocarbon solvents, styrene, and coal tar chemicals. Each contributes its own reports.

The most important academic database is that of the Institute of Scientific Information (ISI), known as the *ISI Web of Knowledge* (www.isinet.com/isi).

Starting with a science citation index, they now also operate social science, and arts and humanities indexes. Membership of a subscribing institution is necessary. The NIST Chemistry Webbook (webbook.nist.gov/chemistry) is open to all and provides chemical and physical property data on over 40,000 compounds.

Finally and extremely useful are the Chemical Company Annual Reports that are published online. Among the color photographs of Chief Executive Officers, nuggets of valuable information are often to be found. They can all be accessed by search engine.

CHAPTER 1

The Evolution of the Organic Chemicals Industry

The United States, Western Europe, and Japan are the most complex societies that have ever existed. Division of labor has been carried to the point where most people perform highly specialized tasks and rely on many others to provide them with the goods and services they need. In return for these goods and services, they provide their outputs to satisfy the needs of others. All men are brothers in a material sense just as they should be in a moral sense.

The various segments of the economy are interrelated in a complex way. For example, manufacturing industry draws heavily on the output of the mining sector by buying iron ore from which to make steel. In turn, it may convert that steel to machinery to sell back to the mining industry where it will be used in mining operations.

1.1 THE NATIONAL ECONOMY

The interdependence of a society's activities may be seen more clearly if its economy is divided into specific industries or groups of industries. Until 1997 this was done according to the standard industrial classification (SIC) of the U.S. Bureau of the Census, but this has now been revised as the North American Industry Classification System (NAICS). Table 1.1 shows the main sectors of a developed economy. The manufacturing sector is designated sections 31–33. Each industry within it is allocated a three-digit code number, chemical manufacturing being 325. Sectors, subsectors, and sub-subsectors of the industry are then allocated four-, five-, and six-digit numbers. For example, Basic Chemical Manufacturing is 3251, Dyes and Pigments are 32513, and Synthetic Organic Dyes and Pigments are 325132. Broadly speaking, the basic chemical industry (NAICS 3251) isolates or synthesizes chemicals, whereas the allied products industries (NAICS 3252–3259) modify,

TABLE 1.1 Main Sectors of a Developed Economy

NAICS Classification (2007)	The Economy	NAICS Classification (2007)	The Economy
11	Agriculture, Forestry, Fishing and Hunting	53	Real Estate and Rental and Leasing
21	Mining, Quarrying, and Oil and Gas Extraction	54	Professional, Scientific, and Technical Services
22	Utilities	55	Management of Companies and Enterprises
23	Construction	56	Administrative and Support and Waste Management and Remediation Services
31–33	Manufacturing	61	Educational Services
42	Wholesale Trade	62	Health Care and Social Assistance
44–45	Retail Trade	71	Arts, Entertainment, and Recreation
48–49	Transportation and Warehousing	72	Accommodation and Food Services
51	Information	81	Other Services (except Public Administration)
52	Finance and Insurance	92	Public Administration

Source: United States Census Bureau, Annual Survey of Manufacturers 2010.

formulate, and package products based on those chemicals. The NAICS codes for the chemical industry are shown in Table 1.2.

The combined value of shipments is the total sales of the industry. Value added is defined as the value of shipments less cost of raw materials and cost of manufacture (Appendix A). Value added per employee is the productivity. Among the specific items in the cost of manufacture are containers, fuels, purchased electricity, bought-in services, and contract work. It is thus the value added to all the inanimate inputs to an industry by the people working in it. The total value added throughout the economy is the gross national product (GNP), the sum of wealth produced by the nation, in this case about \$14.35 trillion for the United States in 2009, amounting to \$46,740 per person.

The manufacturing sector contributed about \$2.3 trillion of value added, which was about a sixth of that year's GDP (gross disposable product = GNP – net income from abroad). The figure has dropped from about 40% in the past generation. This underscores the point that manufacturing, the traditional means for creating wealth, is no longer the major part of our national economy and has to some extent been replaced by services.¹ A similar shift has occurred in Europe and the data are shown in Figure 1.1.

TABLE 1.2 Breakdown of Manufacturing Category NAICS 31–33 (2009^a)

NAICS-Based Code	Meaning of NAICS-Based Code	Number of Employees (thousands)	Total Value of Shipments (thousands)	Value Added (\$ billion)
31–33	<i>Manufacturing 2008</i>	12,748	5,468.0	2,266.0
31–33	Manufacturing 2009	11,051	4,436.2	1,978.0
311	Food manufacturing	1,394	628.6	258.6
312	Beverage and tobacco product manufacturing	142	119.9	71.0
313	Textile mills	109	26.5	11.4
314	Textile product mills	112	21.3	9.1
315	Apparel manufacturing	114	14.7	6.9
316	Leather and allied product manufacturing	28	4.2	2.1
321	Wood product manufacturing	352	65.4	25.9
322	Paper manufacturing	364	161.8	76.5
323	Printing and related support activities	509	83.9	50.5
324	Petroleum and coal products manufacturing	102	497.9	78.6 ^b
325	Chemical manufacturing	725	628.9	328.9 ^b
326	Plastics and rubber products manufacturing	673	171.2	82.3
327	Nonmetallic mineral product manufacturing	360	90.4	48.9
331	Primary metal manufacturing	355	168.3	48.2
332	Fabricated metal product manufacturing	1,297	281.3	146.9
333	Machinery manufacturing	962	287.6	133.1
334	Computer and electronic product manufacturing	908	328.0	193.2
335	Electrical equipment, appliance, and component manufacturing	353	106.7	50.5
336	Transportation equipment manufacturing	1,240	545.0	229.6
337	Furniture and related product manufacturing	360	60.8	32.2
339	Miscellaneous manufacturing	592	143.9	93.7

^a The 2009 statistics were the latest available (U.S. Census Bureau, Annual Survey of Manufacturers, 2010) when this chapter was prepared. However, 2009 was a year of recession and the figure for all manufacturing in 2008 is given at the top of the table.

^b Contrast the value added of the petroleum industry (\$78.6 billion) with that of the chemical and allied products industry (\$328.9 billion). The chemical industry's value added is 4.2 times as great despite the fact that its sales are only one-quarter higher. It is this greater value added that motivated the petroleum companies to develop chemical arms.

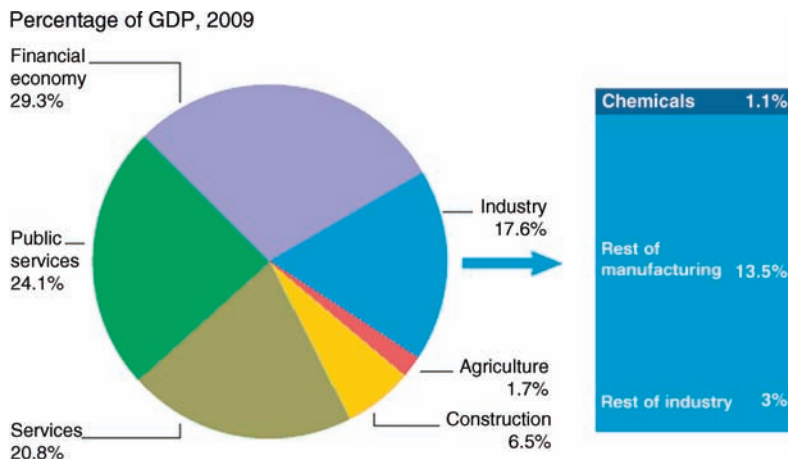


FIGURE 1.1 Services make up almost half of the European Union GDP. Manufacturing makes up 13.5% and chemicals 1.1%. (Source: CEFIC.)

In 1991 the chemical industry provided the largest amount of value added among manufacturing industries and, while surrendering the position briefly, it was firmly in position by 2009 (a bad year). Its main competition has been from Food Manufacturing (311), Transportation Equipment (336) and Computers and Electronic Products (334). In shipments, in 2009, it tied with Food Manufacturing (311) and was followed by Transportation Equipment (336), Petroleum and Coal Products (324), and Computers and Electronic Products. The Chemical Industry ranks only sixth in the number of employees. Value added per employee is the usual measure of productivity, and here the chemical industry ranks third after *Beverage and Tobacco Products* and *Petroleum and Coal Products*.

These data are shown in Figure 1.2.

1.2 SIZE OF THE CHEMICAL INDUSTRY

The world chemical industry produced sales of about \$3 trillion in 2008 (1871 billion euros in 2009); the euro:dollar exchange rate varied between 1.2 and 1.4 over these years). It provided jobs directly for more than 7 million people and indirectly for 20 million. The division by product sector is shown in Figure 1.3 and by region in Figure 1.4. The United States accounted for about 21% of this business, the European Union (25 countries) for 24%, and Japan for about 6.4%. Asia-Pacific, a relative newcomer, accounted for 38% if Japan is excluded. Other regions are much less significant. Fourteen years ago, the United States accounted for a third and Japan for about 15%, so there has been a huge swing to Asia-Pacific. This will be discussed in Chapter 2. During the previous 10 years, world trade in chemicals grew more than 1.6 times faster than that of global output and has risen to an estimated €970 billion (US\$ 1.2 trillion). Almost 45% of the value of the global chemical industry is traded, and more than 35% of this world trade is intracompany in nature.

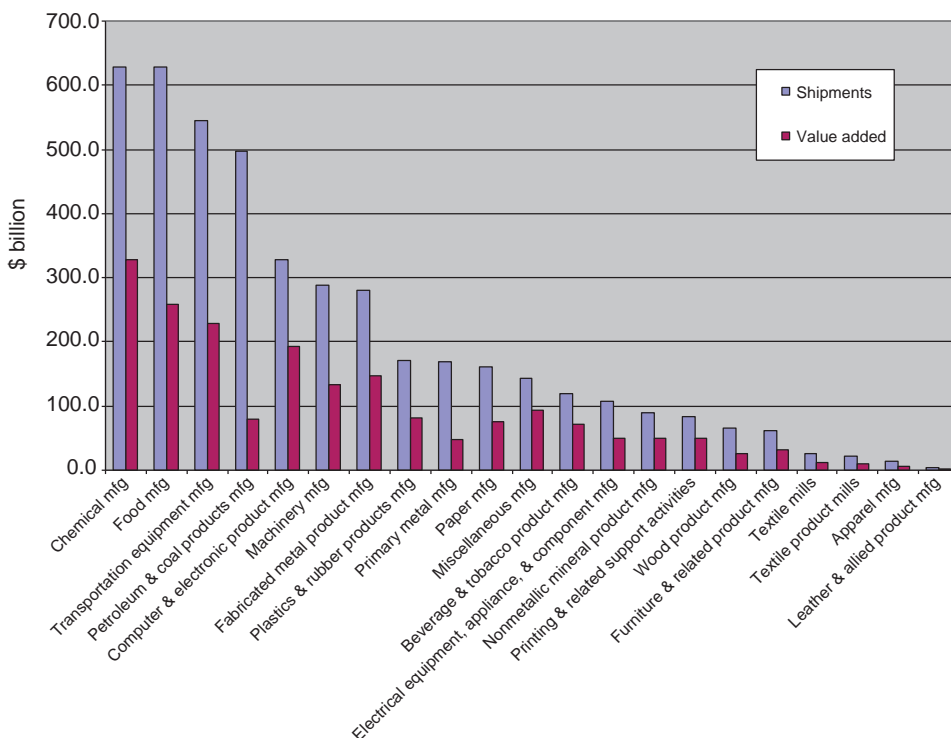


FIGURE 1.2 Shipments and value added in manufacturing industry, United States 2009. (Source: U.S. Bureau of the Census.)

EU 27 embraces the expanded European community including the 12 Eastern European countries recently admitted. NAFTA is the North America Free Trade Organization – the United States, Canada, and Mexico. “Rest of Europe” includes Switzerland, Norway, and the Central and East European countries not in the EU; “Other” is Oceania and Africa.

Figure 1.3 shows that commodity chemicals (inorganics plus petrochemicals) make up half the global market with specialties (life science and performance chemicals) making up the other half. Performance chemicals include specialty surfactants, electronic chemicals, specialty adhesives and sealants, explosives, catalysts, cosmetic additives, dyes and pigments, flavors and fragrances, specialty lubricants, oil field chemicals, paint additives, photographic chemicals, photovoltaic chemicals, plastics additives, and water treatment chemicals. Life science chemicals include pharmaceuticals, agrochemicals, fine chemicals, animal health products, nutritional products and vitamins, diagnostic substances, and biological products.

The division by sector, although the categories do not match NAICS categories precisely, suggests that the world pattern is close to the U.S. pattern. For example, NAICS 32532 + 32541 (pharmaceuticals and agrochemicals) comes to 27.7% compared with life science chemicals at 28%; inorganics (32512 + 32518 + 32534)

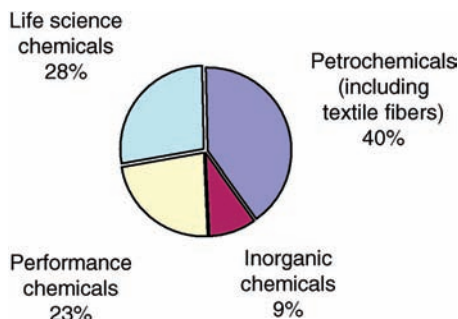


FIGURE 1.3 World chemical market 2008: total \$3 trillion.

comes to 9.1% compared with 9%; and petrochemicals + textiles (32511 + 32519 + 3252) comes to 39% compared with 40%. This is perhaps surprising in that one would expect the United States to have a higher proportion of sales of the higher value specialties.

The U.S. industry had sales of about \$300 billion in 1992, \$460 billion in 2000, and \$751 billion in 2008. The division by shipments is shown in Figure 1.5 and Table 1.3, which also show the division by value added. Petrochemical manufacturing has easily the highest value added per employee, reflecting the small labor force required to operate the huge, semiautomatic cracking units. The same, but to a lesser extent, applies to fertilizer manufacturing, which is based on huge ammonia plants.

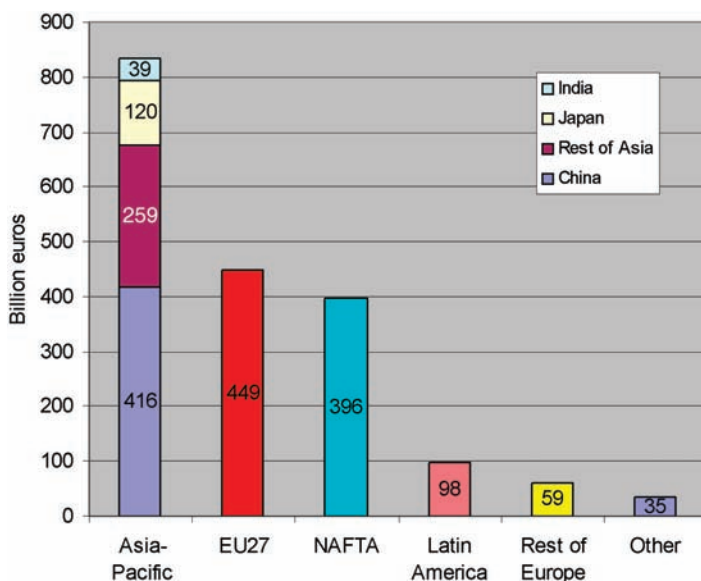


FIGURE 1.4 World chemical market by region (2009); total 1871 billion euros. (Source: CEFIC Chemdata International.)

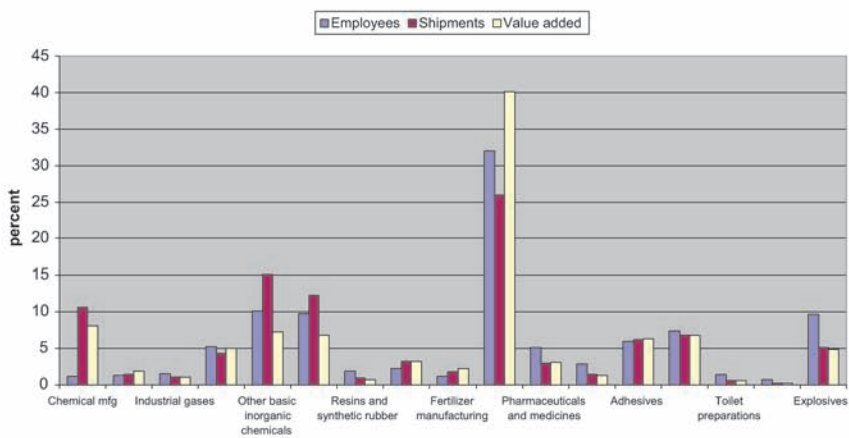


FIGURE 1.5 Subdivisions of the chemical industry by employees, sector, and value added.

TABLE 1.3 United States Chemical Industry 2008

NAICS-Based Code	Meaning of NAICS-Based Code	Number of Employees	Shipments (\$1000)	Value Added (\$1000)	Shipments (%)	Value Added (%)	Value Added per Employee (\$1000)
325	Chemical manufacturing	780,127	751,029,562	355,480,721			456
3251	Basic chemical manufacturing	151,839	244,174,295	83,628,920	32.5	23.5	551
32511	Petrochemical manufacturing	9,376	79,381,904	29,050,222	10.6	8.2	3098
32512	Industrial gas manufacturing	10,622	10,359,554	6,870,257	1.4	1.9	647
32513	Synthetic dye and pigment manufacturing	11,763	7,694,134	3,819,730	1.0	1.1	325
32518	Other basic inorganic chemical manufacturing	40,788	32,719,979	17,975,082	4.4	5.1	441
32519	Other basic organic chemical manufacturing	79,289	114,018,724	25,913,629	15.2	7.3	327
3252	Resin, synthetic rubber, and artificial synthetic fibers and filaments manufacturing	91,176	99,325,574	26,639,741	13.2	7.5	292
32521	Resin and synthetic rubber manufacturing	76,471	92,177,651	24,055,550	12.3	6.8	315
325211	Plastics material and resin manufacturing	67,410	83,802,525	21,728,853	11.2	6.1	322
325212	Synthetic rubber manufacturing	9,061	8,375,126	2,326,698	1.1	0.7	257
32522	Artificial and synthetic fibers and filaments manufacturing	14,705	7,147,924	2,584,191	1.0	0.7	176
3253	Pesticide, fertilizer, and other agricultural chemical manufacturing	27,807	38,225,928	19,650,880	5.1	5.5	707
32531	Fertilizer manufacturing	18,110	24,425,450	11,413,127	3.3	3.2	630
32532	Pesticide and other agricultural chemical manufacturing	9,698	13,800,477	8,237,753	1.8	2.3	849

3254	Pharmaceutical and medicine manufacturing	249,121	194,478,397	142,772,617	25.9	40.2	573
325411	Medicinal and botanical manufacturing	24,395	9,556,348	5,598,245	1.3	1.6	229
325412	Pharmaceutical preparation manufacturing	160,124	149,178,418	110,946,915	19.9	31.2	693
325413	Invitro diagnostic substance manufacturing	26,973	12,701,625	8,619,950	1.7	2.4	320
325414	Biological product (except diagnostic) manufacturing	37,629	23,042,007	17,607,507	3.1	5.0	468
3255	Paint, coating, and adhesive manufacturing	62,630	32,829,586	15,739,772	4.4	4.4	251
32551	Paint and coating manufacturing	40,407	22,418,425	11,012,013	3.0	3.1	273
32552	Adhesive manufacturing	22,223	10,411,162	4,727,759	1.4	1.3	213
3256	Soap, cleaning compound, and toilet preparation manufacturing	104,436	97,431,042	46,661,275	13.0	13.1	447
32561	Soap and cleaning compound manufacturing	46,880	46,510,389	22,615,247	6.2	6.4	482
32562	Toilet preparation manufacturing	57,556	50,920,652	24,046,027	6.8	6.8	418
3259	Other chemical product and preparation manufacturing	93,117	44,564,740	20,387,516	5.9	5.7	219
32591	Printing ink manufacturing	11,242	4,424,392	2,007,833	0.6	0.6	179
32592	Explosives manufacturing	6,042	1,934,663	977,496	0.3	0.3	162
32599	All other chemical product and preparation manufacturing	75,833	38,205,685	17,402,188	5.1	4.9	229

Source: U.S. Census Bureau, American Factfinder.

Comparison of the shipments and value added in Figure 1.5 shows that “fine chemicals,” such as pharmaceuticals, pesticides, and toilet preparations, make a larger contribution to the chemical industry’s value added than they do to its shipments. They tend to be high-priced products with specialized markets, and their manufacture is less capital- and more labor-intensive than the manufacture of the run-of-the-mill general chemicals. Their importance to the chemical industry is best represented by the value-added figure, which, for example, emphasizes the overwhelming importance of the pharmaceutical sector, which accounts for 25.9% of shipments but 40.2% of value added.

The total chemicals sector in the United States grew by 3.5%/year between 1991 and 2001 but by only 0.9%/year between 1999 and 2009. The basic chemicals sector shrank by 0.4%/year between 1999 and 2000 and the organic chemicals sector shrank by 0.2%/year over the same period. Thus the organics chemicals sector showed lackluster performance over the 1990s and early 2000s. Production dipped dramatically in 2001 and recovered strongly, reaching a peak in 2007 but slumping by about 20% in the following two years. At the time of writing, a 2010 recovery is probable, but the chemical industries of the Western world and Japan have had a difficult two decades, in contrast to the vigorous growth of earlier years.

1.3 CHARACTERISTICS OF THE CHEMICAL INDUSTRY

The chemical industry has certain well-defined characteristics that govern its attitudes and performance. These are listed in Table 1.4; we shall discuss the first six in this chapter and the remainder in Chapter 2.

1.3.1 Capital Intensity and Economies of Scale

The chemical industry is capital intensive. It produces huge quantities of homogeneous materials, frequently liquids or gases, which can be manufactured, processed, and shipped most economically on a large scale. This was less so through the nineteenth century until World War II. The early chemical industry used more general

TABLE 1.4 Characteristics of the Chemical Industry

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1. Capital intensity and economies of scale
 2. Criticality and pervasiveness
 3. Freedom of market entry
 4. Strong regulation of health and safety issues
 5. High but declining research and development expenses
 6. Dislocations
 7. Maturity and its consequences (restructuring, mergers, demergers, acquisitions)
 8. Participation in international trade
 9. Competition from the developing countries
-

purpose equipment and operated batch processes that required little capital investment but had high labor costs. Typical of such processes were the Leblanc route to sodium carbonate and the benzenesulfonate route to phenol (Section 9.1).

The petroleum refining industry was the first to convert to continuous operation on a large scale. The engineering developed for the petroleum industry was applied to the chemical industry after World War II. Plant sizes escalated as dramatic economies of scale became possible. The capacity of a typical ethylene cracker rose from 32,000 metric tons per year in 1951 to 450,000 metric tons per year in 1972. This was regarded as an upper size limit until the early 1990s when plants with 680,000 metric tons per year capacity were built. Meanwhile, in 2001, BASF/Fina brought on stream a 900,000 metric ton ethylene plant in Port Arthur, Texas, and SABIC has built a 1,200,000 metric ton plant at Al Jubail on the Gulf Coast of Saudi Arabia. The Port Arthur plant will incorporate a metathesis unit described in Section 4.14. Even the residual butadiene/isobutene will make this the world's largest C_4 olefins plant.

Currently there are few batch processes of any size in operation for commodity chemicals, and substantial economies of scale are a characteristic of the petrochemical industry. They arise not only from improved technology but also from purely geometric factors. The capacity of a great deal of chemical equipment (e.g., storage tanks and distillation columns) varies with its volume, that is, the cube of its linear dimensions. The cost, on the other hand, is the cost of a surface to enclose the volume and varies with the square of the linear dimensions. Consequently, cost is proportional to (capacity)^{2/3}. This is called the square-cube law. It does not apply to all equipment. The capacity of a heat exchanger depends on its surface area so cost is proportional to (capacity)¹ and there are no economies of scale. Control systems are not affected by capacity at all, so cost is proportional to (capacity)⁰ and economies are infinite. It is claimed that for a modern petrochemical plant overall, cost is proportional to (capacity)^{0.6}.

Labor costs are a small proportion of petrochemical plant cash costs (HDPE 2.5%, benzene 3.5%, purified terephthalic acid 5.7%, acrylonitrile 7.3%) but they contribute to economies of scale, because they do not increase proportionately to increase in size of the plant. Doubling the size of a unit does not double labor cost. Indeed, because of automation, the labor cost may increase only 10–20%.²

The size and complexity of a modern chemical plant demand high capital investment. Although other industries invest more capital per dollar of sales, the chemical industry has the highest investment of current capital. That means that the chemical industry invests more each year than do other capital-intensive industries such as mining, where equipment once bought remains in service for many years.

Capital intensity has a number of corollaries. The return on capital is relatively low. Because high capital investment reduces the labor force required, manpower productivity (i.e., value added per employee) is high, while salaries contribute relatively little to costs (on the order of 2.0% for steam crackers). For example, in 2008, in the labor-intensive food manufacturing industry (NAICS 311) the average production worker added value of \$171,000 and was paid \$36,000. In the petrochemical industry (NAICS 32511) the value added per employee was \$3.1 million and the pay \$93,000.

Thus employers need worry less about pay increases and labor relations are unusually good. If we take figures for overall industries, the chemical industry ranked third with a value added of \$454,000/employee after Petroleum and Coal Products (\$774,000) and Beverage and Tobacco Products (\$499,000). Right at the bottom of the list comes the labor-intensive Apparel and other Textile Products Industry with a figure of only \$61,000.

The assets of a company are the estimated value of the plants, land, and other capital goods it owns. Such ratios as assets per employee, sales per dollar assets, and sales per employee are measures both of the capital and labor intensity of an industry.

Generally, the petroleum refining industry has both the highest assets and the highest sales per employee. The chemical industry shows lower figures, but still ranks high. The food and clothing industries are usually at the low end of the scale. Service industries with few assets and many employees, such as consulting companies, will show both low assets and low sales per employee.

The move to specialty chemicals has altered these perceptions as far as the overall chemical industry is concerned, although not for the sectors described in this book. Small, high value, low tonnage chemicals are frequently made by batch processes in multipurpose computer-controlled equipment. Such equipment brings some of the advantages of continuous processing to batch processes.

1.3.2 Criticality and Pervasiveness

A chemical industry is critical to the economy of a developed country. In the nineteenth and first half of the twentieth century, a nation's industrial development could be gauged from its production of sulfuric acid, the grandfather of economic indicators. Today one uses ethylene production as a yardstick of industrial sophistication. An advanced economy cannot exist without a chemical industry; neither can a sophisticated chemical industry exist without an advanced economy to support it and to provide the educated personnel it requires. Nevertheless, various developing countries have started to build chemical industries by buying "turnkey" plants constructed by foreign chemical engineering contracting companies and staffing them either with imported foreign labor or with locals who have been educated abroad. Indeed this is part of the development process.

The chemical industry is an "upstream" industry. It purchases raw materials such as petroleum, natural gas, coal, and metallic and nonmetallic minerals. In 2008, the U.S. industry purchased raw materials for \$396.7 billion and converted them to products that it sold for \$751.0 billion. Apart from pharmaceuticals, these products are usually not sold to the final consumer. About a quarter of them are sold to other firms in the chemical industry for further processing. The remainder is sold to other industries to help them make their own products or sell their services. Makers of plastic packaging, for example, rely on polymers. Automobile manufacturers use the products of chemical industry in tires, hoses, safety glass, seat belts, upholstery, bumpers, fenders, and even doors and side panels as well as many other components. The pattern in 2007, which is the most recent set of data, is shown in Figure 1.6. Having said that chemicals is an upstream industry, we need to explain the half of

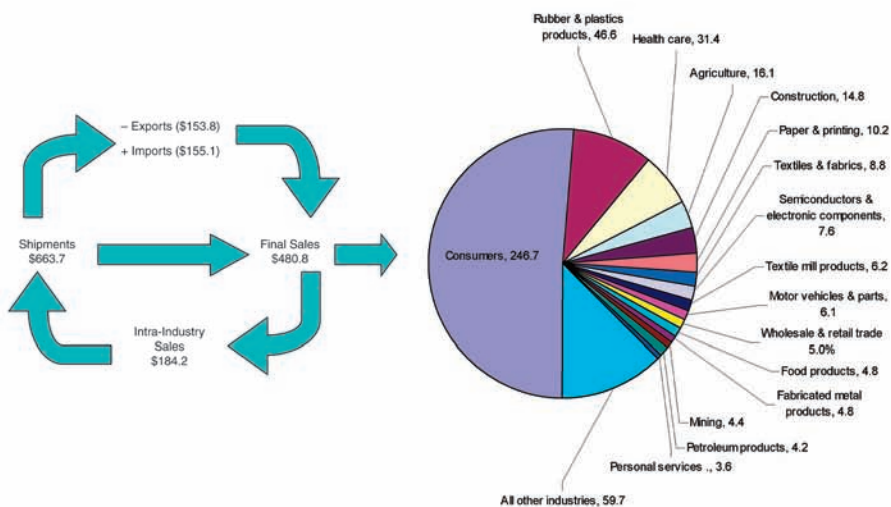


FIGURE 1.6 Who buys chemicals? (United States, 2007) (Source: ACC analysis based on Bureau of the Census, Bureau of Economic Analysis, and Bureau of Labor Statistics.)

output that goes to consumers. About two-thirds of this is pharmaceuticals, which are classified under the chemical industry heading. The remainder is products of the soap, detergents, and cosmetics sector together with domestic paints. If pharmaceuticals are excluded, the “upstream” nature of the chemical industry is clearer.

The chemical industry was always said to be its own best customer, but the \$184.2 billion intra-industry sales in 2007 were probably slightly smaller than the sales of the pharmaceuticals sector. Thus the pharmaceutical industry (if it is not classified as part of the chemical industry) is the major purchaser by value, although certainly not by volume. It buys small quantities of high value-added chemicals. Rubber and plastics producers buy large quantities of resins and the textile industry buys synthetic fibers. Petroleum refiners, who supply much of the industry’s raw materials, also buy back some of its products to aid their own processing.

The chemical industry is not replaceable. There is no other industry that could fulfill its function. It is pervasive and reflected in all goods and services. Not only is the chemical industry here to stay, but also it is a dynamic and innovative industry that has grown rapidly and on which the world will continue to rely in the future. Many of the problems concerning pollution and energy have been detected and monitored by chemical methods, and chemistry is playing a part in their solutions.

1.3.3 Freedom of Market Entry

Another characteristic of the chemical industry is freedom of market entry. Anyone who wants to manufacture bulk chemicals may do so by buying “turnkey” plants. Chemical engineering contracting companies have processes for preparation of virtually any common chemical and will build a plant guaranteed to operate for anyone who wishes to invest the money. This was the way that many of the petroleum companies gained entry to the petrochemical business and is also the route followed by developing countries.

The one requirement is large amounts of capital. To enter the basic chemical business requires a bare minimum of \$1 billion. Large sums of money may be required for purposes other than capital investment. In the pharmaceutical industry, large sums are required for research and development, which in the early 2000s was \$500–1000 million per drug. The detergent industry, on the other hand, requires money for massive amounts of advertising. These two industries underscore the importance of large cash flows to support research and development and merchandising. Thus entry into the chemicals market is free in the sense in which economists use the word, but the expense is such that only governments, oil companies, and other giant enterprises can find the necessary capital.

What has been said about capital applies primarily to very large volume basic chemicals such as the seven basic chemical groups (Table 4.1) and their first-line derivatives. Beyond that there may be other barriers to entry such as lack of necessary technology or reluctance on the part of a patent holder to license technology. An example is DuPont’s process for making hexamethylenediamine by the hydrocyanation of butadiene (Section 7.1.6). The process was invented by DuPont but was sold by them to Koch, the second largest private company in the United States. Its economics

make it the preferred process, but it is not available for license. On the other hand, the Dutch company Akzo was able to enter the Aramid (DuPont's Kevlar) business, presumably by finding loopholes in the DuPont patents. Kevlar (Section 11.3.4) is used for fibers that are stronger, weight for weight, than steel and DuPont finds it profitable, but the business had to be shared with Akzo since the patents were apparently not invincible. The competition was further intensified by DSM's Dyneema, a strong fiber based on very high molecular weight polyethylene and also used for body armor but not for high temperature applications.

Downstream operations may provide a barrier to entry. Thus the manufacturers of poly(methyl methacrylate) conventionally convert their product to acrylic sheets, which are then sold to molders. Potential manufacturers must decide whether they want to gain the expertise that participation and marketing the sheet requires. Indeed, will the company's culture allow participation in a business so far removed from basic chemical manufacture?

Low price of the product, and correspondingly low profitability, may deter entry. Furfural (Section 16.2.1) provides a classic example. When introduced many years ago, it was priced so low that it never attracted competition until well into the product's life cycle, and then major competition came not from U.S. companies but from China. Companies with products whose patents are about to expire often use this technique to discourage other manufacturers. Monsanto used it successfully when one of its herbicides came out of patent. It was able to manufacture it cheaply in a depreciated plant by an optimized process. It was not worthwhile for other companies to invest the fresh capital in order to compete. And, to Monsanto's surprise, the market increased as farmers used more of this cheap herbicide to control weeds in place of the more cumbersome processes of plowing or covering the ground with plastic. Union Carbide similarly exploited the technique with its pesticide carbaryl (Section 12.5.2.6). By pricing it low, it successfully avoided serious competition after the patent had expired.

1.3.4 Strong Regulation

The chemical industry is one of the most highly regulated of all industries. The regulations are intended to protect and improve the worker's and the nation's health, safety, and environment. Chemicals may be toxic or hazardous, that is, they may be liable to poison people fairly quickly or to catch fire or to explode. Some chemicals may appear to damage the environment in ways that are subtle and not well understood. These are the problems that arouse the greatest debate. Long-term ill effects may not be evident or demonstrable in the short term, and in the long term it will be too late to do anything.

The regulatory environment of the chemical industry is subdivided in a number of ways and monitored by various government departments and agencies, some of which are shown in Table 1.5. The on-site problems of regulating the manufacture of chemicals are dealt with mainly by the Department of Labor under the Occupational safety and Health Act, although the Food and Drug Administration sets up standards for Good Manufacturing Practice (GMP), especially in the pharmaceuticals industry. The on-site chemicals may be intermediates that are being processed further, raw

TABLE 1.5 Who Monitors the Chemical Industry?**Environmental Protection Agency (EPA)**

Clean Air Act (CAA)	41 pollutants had to be controlled by 1995; 148 more by 2003. Cost to industry estimated at \$25 billion per year
Federal Insecticide, Fungicide, Rodenticide Act (FIFRA)	
Pollution Prevention Act (PPA)	
Resource Conservation and Recovery Act (RCRA)	Clean up of hazardous and nonhazardous waste sites. Cost to industry \$9–60 billion in decade 1990–2000.
Safe Drinking Water Act (SDWA)	Sets standards for 83 chemicals in water
Clean Water Act (CWA)	Ensures high quality water
Toxic Substances Control Act (TSCA)	Requires premanufacture notification to EPA of tests on and effects of new products
Food Quality Protection Act (FQPA)	
Superfund Amendments and Reauthorization Act (SARA)	Clean up of hazardous sites. Mostly funded by taxes in industry.
Comprehensive Environmental Response Compensation and Liability Act (CERCLA)	

Food and Drug Administration (FDA)

Federal Food, Drug and Cosmetics Act	Sets standards for and evaluates tests of food, drugs and cosmetics.
Good Manufacturing Practice	Center for Drug Evaluation & Research imposes standard.

Department of Labor

Occupational Safety and Health Act (OSHA)	Defines hazards in an attempt to prevent industrial accidents. Defines permissible exposure limits for 600 hazardous chemicals.
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Department of Transportation

Hazardous Materials Transportation Act

Department of Justice

Chemical Diversion and Trafficking Act (CDTA)	Prevents use of chemicals to make illegal drugs
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Other Departments

Poison Packaging Prevention Act (CPSC)	
The Emergency Planning and Community Right-to-Know Act	Reporting of production, handling and storage of hazardous materials
State Laws and Regulations	

materials and end products that are being stored, or effluents that are being discharged into the environment. GMP is of particular interest in that it not only sets standards for cleanliness, hygiene, and exposure to toxic substances in the pharmaceutical industry, it also insists on specific documentation and demands specific management

structures. For example, the heads of production and quality control must be independent of each other.

In a worldwide industry in which many countries are participating, there are bound to be accidents. A list of serious accidents over the decade 2000–2010 is shown in Table 1.6. At first sight, this is a long list but there have been no countries with more than two accidents over the ten-year period. The desirable level of accidents is, of course, zero, but in comparison with the petroleum and nuclear industries, the record of the chemical industry is very good. All three industries are far safer than such mundane activities as fishing and mining. Meanwhile, chemical industry executives must pray nightly that there will never be another Bhopal. The absence of major plant accidents in recent years does not mean that the potential for such accidents does not exist. Plant safety is a matter of trying to learn from the accidents that do happen.

Chemicals need not only to be produced safely but also shipped safely. The problems of shipping chemicals are regulated by the Department of Transportation, while the problems associated with the off-site use of chemicals are largely the responsibility of the Environmental Protection Agency. The off-site chemicals may be materials that are themselves toxic or hazardous, or there may be problems arising from their use or disposal. In the former category come many pharmaceuticals that are toxic in large doses and in the latter such materials as chlorinated hydrocarbons and nonbiodegradable plastics.

1.3.4.1 European Legislation

Legislation from the European Commission came into force on 1 June 2007 under the acronym REACH (Registration, Evaluation and Authorization of Chemicals). It is having a major impact on the European chemical industry and on external companies that trade with Europe. By extension, it is likely that other countries such as the United States and Japan will introduce similar regulations; indeed the Toxic Substances Control Act is currently under review. The stated aims of REACH are to ensure a high level of protection of human health and the environment from the risks that can be posed by chemicals, the promotion of alternative test methods, the free circulation of substances on the internal market, and enhancing competitiveness and innovation. The catch is that the industry is made responsible for assessing and managing the risks posed by chemicals and providing appropriate safety information to their users. In contrast to the U.S. Toxic Substances Control Act, which only applies to chemicals newly coming into use, REACH applies to all chemicals imported or produced in the EU. It does not apply outside the EU and does not apply to foodstuffs.

By the December 2008 deadline, an incredible 143,000 chemical substances had been registered as being imported or produced on a scale greater than one metric ton. These are all to be tested for safety and toxicity. The Commission proposes the review and registration of 30,000 dossiers followed by a more detailed evaluation (risk and hazard assessment) of 5000 of them, including all those produced at volumes greater than 100 metric tons/year. Of the 5000, about 500 are expected to be classified as carcinogenic, mutagenic, or reprotoxic and these, plus another 859 chemicals “of high concern,” will have to be authorized before use. The deadline for chemicals

produced on a scale of >1000 metric tons/year is 30 November 2010, >100 metric tons/year 1 June 2013, and >1 tonne/year 2018. The exercise is predicted to cost the European chemical industry 9.5 billion euros (\$12.4 billion) over the next decade and cost the lives of 54 million vertebrates, although other commentators say this is a sixfold exaggeration.^{3,4} Thus the “green” supporters of better chemical testing are at the throats of the equally “green” animal rights activists.

The proposals are intended to share the costs and responsibilities of testing between the indigenous producers and also non-European companies who wish to export to Europe. The consortium cost for authorization of hydrogen chloride came to 881,000 euros (\$1.15 million) and was shared among 70 members. Only one set of animal tests is permitted per chemical, so companies are forced to come together and to share information. Unfortunately, this may contravene EC legislation on cartels, an issue that remains to be settled.

The spokespeople for the European chemical industry see the new regulations as a bureaucratic albatross hung around their necks by the austere Scandinavians, as opposed to the easy-going Mediterranean peoples. They feel that European legislators think of the world as it was in 1900, with everyone under their benevolent rule, except for the Americans, who had inexplicably escaped. In reality, the Americans are modifying the Toxic Substances Control Act to make it closer to REACH.

Meanwhile, Europe is increasingly less significant, and the Europeans might well find themselves left as a quiet backwater while the United States, Japan, China, and India get on with running the world. Equally, Greenpeace and the other environmentalists feel that the new regulations do not go far enough, and that the wicked chemical industrialists will find a way of maintaining or even increasing their profits in spite of the legislation.

1.3.4.2 Political Factors

With such a battery of regulatory agencies, the chemical industry might hope that the general public would view its activities benevolently. The reverse is the case, and the chemical industry is regarded with fear and suspicion by many. In fact, as noted above, it is a remarkably safe industry. The truly dangerous activities are such things as smoking cigarettes or crossing the road. The perceived danger of the chemical industry has four reasons. First, people are not familiar with the operations carried out in a chemical plant. The risks inherent in working on high buildings are evident and, when workers fall from them, the accident is seen as regrettable but inevitable. Second, accidents in chemical plants are infrequent but, when they occur, they are spectacular (Table 1.6). The same applies to airplane accidents, hence many people's fear of flying. If the number of people who are killed on the roads every week died simultaneously in a weekend catastrophe, motor vehicles would probably be banned. Third, the chemical industry is an “upstream” industry and people are unfamiliar with its products and unaware of the extent to which they depend on them. Chemicals are ubiquitous but invisible to the public. Fourth, they worry that they are being poisoned insidiously by the products of the chemical industry without their knowing anything about it.

TABLE 1.6 Chemical Industry Disasters 2000–2010

Date	Accident	Dead/Injured
4 October 2010	The dam of Magyar Aluminium Zrt's red mud reservoir broke and the escaping highly toxic and alkaline (~pH 13) sludge flooded several settlements.	9 dead/hundreds burned by alkali
13 November 2005	Explosions at Jilin Petrochemical's aniline plant leaked 100 metric tons of aniline, benzene, and nitrobenzene into the 1850 km Songhua River.	5 dead/main water source in northeastern China polluted
23 March 2005	Explosion and fire at BP's Texas City refinery during the start-up of an isomerization unit.	15 dead/>170 injured
25 February 2005	Petrochemical plant of Jaingsu Tiantin Chemical Industry in eastern China suffers an explosion.	5 dead/11 injured
1 September 2004	Ethylene unit explodes at Sasol's synthetic fuel facility at Secunda, South Africa.	10 dead
25 May 2004	A truck carrying ammonium nitrate overturns and explodes in Mihailesti, eastern Romania.	16 dead/11 injured.
11 May 2004	Explosion at Stockline Plastics' factory in the Maryhill district of Glasgow, UK.	9 dead/>40 injured
23 April 2004	Explosion at Formosa Plastics USA's polyvinyl chloride plant in central Illinois.	5 dead/5injured
19 January 2004	Explosions at three LNG storage tanks at Algerian energy and chemicals group Sonatrach's Skikda complex	30 dead/70 injured
14 October 2003	Explosion at the Gujarat Narmada Valley Fertilizers nitrophosphate production complex at Narmadanagar, India.	5 dead/30 injured
21 September 2001	Explosion in a storage hangar in which 300 metric tons of ammonium nitrate granules were stored for recycling at Atofina Grande Paroisses fertilizer plant in Toulouse in southwest France.	30 dead/>200 injured

Source: Based on <http://www.icis.com/Articles/2005/12/12/1003600/TIMELINE-Major-global-chemical-disasters.html>.

Whereas one can perhaps avoid being knocked down by a taxicab by taking care, people fear that undetectable chemicals are being ingested with food or water, breathed in with air, or absorbed through the skin. The life cycle of many chemicals is not understood, and the view that we are all being slowly poisoned has inspired various attacks⁵ and defenses.⁶ Brominated flame retardants from television sets, for example, are said to occur in sperm whale body fat, but how they get there is a mystery (Section 20.4.2.2).

In spite of the REACH legislation, there is no practicable way in which “chemicals” can be proved to be absolutely safe, even in the cases where extensive testing has been carried out. A blanket ban on “chemicals” is, however, out of the question. The products of the chemical industry confer benefits. Urban life would be impossible without food preservatives. Pesticides and rodenticides mean that we are able to feed ourselves adequately rather than having our crops destroyed by animal and insect competitors. Fertilizers enhance crop yields. Modern drugs extend our life spans. Synthetic polymers enable us to live much more comfortably than our ancestors. There is no way in which risks can be eliminated completely, but the chemical industry in the developed world is active in testing the toxicity of the products that it manufactures, tracing the sources of pollution and combating it as demanded by the regulations. The American Chemistry Council, previously the Chemical Manufacturers’ Association (CMA), has documented industry’s vigorous response to the need for pollution abatement. Which chemicals should be permitted and which banned depends (or should depend) on risk–benefit calculations.

To take a few examples, carbon tetrachloride and chloroform are no longer marketed but perchloroethylene is still permitted as a dry cleaning solvent. It has not been classified by REACH as a substance of very high concern, and a consortium led by Dow Chemical is applying for authorization and is due to report at the end of 2010. The United States Environmental Protection Agency and the Europeans would like to eliminate it. No adequate replacement has come to light, however, although Micell has launched a chain of dry cleaners who use beverage-grade liquid carbon dioxide and specialty surfactants.

Lead tetraalkyls were banned from gasoline because they led to lead bromide dust in the environment. Instead, octane numbers were maintained by an increase in aromatics content. Fears of benzene’s carcinogenicity then led to the use of methyl-*t*-butyl ether as an octane improver. This has now largely been banned in the United States, because of contamination of groundwater. It has been replaced by other oxygenates and aromatics. At every stage, attempts have been made to minimize risk.

There is no end to the fears. Chlorinated polymers such as poly(vinyl chloride) give dioxins if burned in inefficient incinerators. Many solvent residues are thought to migrate to the stratosphere and damage the ozone layer. Carbon dioxide, the product of every combustion process, is thought to contribute to global warming. Dealing with all these problems comes at a cost. The stringent requirements of the Clean Air Act had the most far-reaching economic impact on the industry, with a cost of \$25 billion per year.

The cost–benefit discussion inevitably becomes politicized. When C. Everett Koop, a former surgeon general, described an environmentalist campaign against diisobutyl and di-2-ethylhexyl phthalates as “The Latest Phony Chemical Scare,” he was denounced, not because his opponents had powerful evidence of their harmfulness, but because they claimed he was funded by the industry.⁷ Koop, who was instrumental in instituting the warning on cigarette packages, said bluntly that the greatest health hazards were not trace chemicals but smoking, excessive drinking, drug use, accidents in the home, unprotected sex, poor nutrition, and lack of exercise. Nonetheless, REACH classed di(2-ethylhexyl) phthalate, butylbenzyl phthalate, and

dibutyl phthalate as “substances of very high concern” and, in 2004 banned their use in certain children’s toys.

Certainly there appear to be cases where regulation seems to have been excessive. Between 1990 and 1993 the United States spent \$42 billion on the removal of asbestos from public buildings compared with the \$40.8 billion total budget of the National Institute of Health. It is almost unbelievable that more was spent on the former than on the latter. The harm that asbestos exposure can do to a school child is tiny compared to other causes of death. The annual death rate from asbestos exposure in schools was 0.005 to 0.093 per year per million at risk.⁸ The chance of death from high school football was 1–6 per year per million at risk, of drowning (ages 5–14) 27 per year per million at risk, and of being run over by a motor vehicle (ages 5–14) 32 per year per million at risk. In assessing the risk from a material, one needs to know both how carcinogenic (or dangerous in other ways) it is and, equally as important, what an individual’s chances are of exposure to the material. Thus the FDA has announced that short-fiber asbestos and dioxins, through harmful, provide little danger to the general population. Asbestos is harmful only to those who are exposed continually to it in the workplace. That said, the continuing, though small number of mesothelioma cases in the United Kingdom, resulting from low level exposure to asbestos in classrooms and workplaces, makes the UK government look parsimonious and uncaring.

Methyl bromide is an example (Section 20.4.1) where a proposed ban is only slowly being implemented because of lack of a reasonable alternative as a soil fumigant. It was nonetheless phased out in the United States in 2005 subject to allowable exemptions (Section 20.4.1). DDT (Section 9.6) is still used in 23 countries because malaria limitation is seen as more important than the thickness of eggshells but, as the material spreads globally, it will affect people who have taken opposite decisions.

The elimination of benzene from gasoline, mentioned above, was an expensive operation. It cost \$150 million and saved perhaps 3–4 lives per year. A life is priceless, but perhaps there are better ways to spend the money. What about vaccinations for poor children or an anti-obesity campaign or cheaper medical care for the indigenous elderly? Environmentalists might reply that the chemical industry would not reallocate the funds to other causes anyway, but many of the causes are government funded, and the opportunity for more cost-effective allocation of resources exists.

People’s fears of unknown chemicals present in barely detectable amounts in the environment may express itself in barely rational ways. An example is the so-called precautionary principle. This has been stated as “When an activity raises threats of harm to human health and the environment, precautionary measures should be taken even if some cause and effect relationships are not fully established scientifically”. While that sounds harmless and, indeed, such an approach is already in place as instanced by the 1958 Delaney Clause overseeing pesticide residues in food, the new approach is clearly intended to be more stringent. Its opponents feel that extreme environmentalists will no longer have to produce statements of damage caused by particular chemicals to have them banned. The necessity to balance upside benefits against downside risks will be lost, as will the concept of “tolerable daily intake.” A widespread press campaign against a “chemical” will be sufficient, together with the statement that there is no way a material can be proved to be totally harmless, and you

can't be too careful. On such logic, Justice Stoughton was quite right to hang the "witches" of Salem. Threats to human health were certainly attributable to witches even if the cause and effect relationships were not established scientifically.

The precautionary principle has been widely adopted across Europe and has been incorporated into the United Nations Biosafety Protocol regulating trade in genetically modified products. It seems gradually to be working its way into U.S. policy. Much rests on how it is interpreted, and the chemical industry and the general public must hope for a balanced approach.

1.3.5 High but Declining Research and Development Expenditures

The chemical industry used to be research intensive. It hired many graduates, peaking at 13.3% of all scientists and engineers in the United States. It has since declined, but there were 84,300 chemists in the United States in 2008 of whom 42% worked in manufacturing industry (Table 1.7). Thirty-four percent of all chemists worked in the chemical industry and this was made up of 19% in pharmaceuticals and 15% in other sectors of the chemical industry. Of the remainder, almost 30% were in professional, scientific, and technical services; 12.4% in federal, state, and local government; and fewer than 5% in education. About 65% of all chemists and chemical engineers in industry are employed by companies who are not in the chemical industry but require the services of chemists. Polaroid, 3M, Bell Telephone, and IBM are examples.

Industrial R&D expenditures in the United States increased impressively by about 70% in terms of current dollars between 1970 and 1990 and chemical R&D more than doubled. By the 1990s and into the 2000s, the rate of growth of chemical R&D spending had slowed. Figure 1.7 shows expenditure in current and constant (2000) dollars. In basic chemicals, it has remained more or less static at about 3% of sales, and 2009 expenditure was 6.5% lower in real terms than in 1990. Pharmaceutical spending rose from 10.4% of sales in 1990 to 14.5% in 2000 and 19% in 2008 but fell back to 16.3% in the 2009 recession.

Other sectors of the chemical industry are far less research oriented. The specialty chemicals sector spends 4–5% of sales on research, basic chemicals and consumer products 2–4%, and fertilizers a miniscule 1%. The plethora of restructuring in the chemical industry in recent years has demoralized research groups and produced opportunities for highly paid managers on short-term contracts to increase cash flow by disbanding research.

The expenditures of some of the top chemical companies in 2009 are shown in Table 1.8. Companies with major pharmaceutical subsidiaries, such as Bayer, spend more on R&D than do the mainline chemical companies. Research-based pharmaceutical companies with few other interests spend 10–25% of sales on research, but the table is compiled, as far as possible, to exclude pharmaceutical sales. True specialty chemical companies have research budgets about a third of those of the pharmaceutical companies. At the other extreme, the major oil companies (e.g., Chevron-Phillips) are involved mainly with commodity chemicals and spend little on research. The average spend on R&D over all manufacturing industries in the United

TABLE 1.7 Employment of Chemists, United States 2008

Industry ^a	2008		
	Employment (thousands)	Percent of Industry	Percent of Occupation
Total employment, all chemists	84.3	0.06	100.00
31–33 Manufacturing	35.2	0.26	41.78
325 Chemical manufacturing	29.1	3.42	34.44
3251 Basic chemical manufacturing	4.1	2.72	4.90
3252 Resin, synthetic rubber, and artificial synthetic fibers and filaments manufacturing	1.7	1.62	2.03
3254 Pharmaceutical and medicine manufacturing	16.4	5.65	19.41
3255 Paint, coating, and adhesive manufacturing	2.1	3.41	2.54
3256 Soap, cleaning compound, and toilet preparation manufacturing	2.4	2.23	2.86
3259 Other chemical product and preparation manufacturing	1.7	1.80	2.03
42 Wholesale trade	2.4	0.04	2.83
424 Merchant wholesalers, nondurable goods	1.9	0.09	2.29
4242 Drugs and druggists' sundries merchant wholesalers	1.0	0.48	1.19
54 Professional, scientific, and technical services	24.7	0.32	29.27
5413 Architectural, engineering, and related services	9.4	0.65	11.13
54138 Testing laboratories	8.3	5.55	9.82
5417 Scientific research and development services	14.3	2.30	16.95
55 Management of companies and enterprises	2.3	0.12	2.71
56 Administrative and support, waste management and remediation services, employment services	2.5	0.03	2.91
61 Educational services, public and private	4.0	0.03	4.77
62 Health care and social assistance	0.9	0.01	1.11
931 Federal government	6.1	0.22	7.21
932 State and local government, excluding education and hospitals	4.4	0.05	5.22

^aIndustries employing fewer than 1% chemists are omitted.

Source: ftp://ftp.bls.gov/pub/special.requests/ep/ind-occ.matrix/occ_xls/occ_19-2031.xls.

States in 2007 was 3.7%, and the chemical industry averaged a healthy-looking 7.9%, but that figure is skewed drastically by the high spend by pharmaceutical companies.

Various companies do not divulge their R&D spending and have been omitted from Table 1.8. It is claimed that private equity companies spend very little on R&D, and

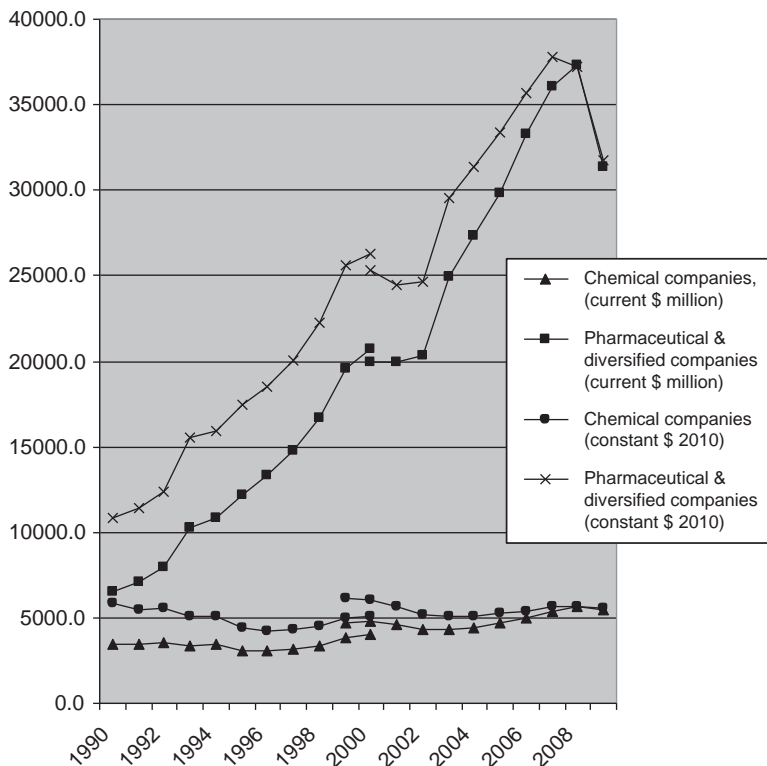


FIGURE 1.7 United States R&D spending. Note the slight mismatch in 1999 and 2000 between earlier and later sets of data. (Source: C&EN 29 October 2001, 26 July 2010.)

Huntsman exemplifies this. Ineos does not disclose its research spending, but Jim Dawson (a director of Ineos) claimed in an interview with Bryan Reuben that he was maintaining the research programs of the companies he had taken over.

Few nonpharmaceutical chemical companies anywhere in the world spend more than the U.S. manufacturing industry average on research, and it is evident that the golden age for industrial chemical research is over, even if expenditure is marginally above the figure for nonchemical companies.

How is the R&D budget spent? Research is a risky and expensive business. Finding the conditions that maximize the cost effectiveness of an R&D budget preoccupies many managers, especially those of pharmaceutical companies. Unfortunately it is not a science, and success in the laboratory often depends on serendipity. Should a company rely on discoveries emerging from the interests of its researchers, or should it try to satisfy the pull of the marketplace? Should it rely on in-house research or should it “out-source” some of its research and look to buy ideas from small entrepreneurial companies? “Technology push” was the initial approach. From 1930 onwards, governments prepared for World War II. R&D received a boost from government tax incentives during and immediately after the war. Much of this

TABLE 1.8 R&D Spending, 2009

Company		Chemical R&D Spending (\$ million)	Percent of Chemical Sales
Syngenta	CH	512	6.1
DuPont	US	1378	5.3
DSM	NL	548	5.0
Shin-Etsu Chemical	J	359	3.7
BASF	D	1930	3.5
Bayer	D	1198	3.5
PPG Industries	US	403	3.5
Dow Chemical	US	1492	3.3
Mitsui Chemicals	J	407	3.2
Arkema	F	190	3.1
Evonik	D	418	3.0
Eastman Chemical	US	137	2.7
AkzoNobel	NL	471	2.4
Solvay	B	194	2.4
Clariant	CH	138	2.3
Tosoh	J	147	2.2
Air Liquide	F	304	2.0
Lanxess	D	141	2.0
Huntsman Corporation	US	145	1.9
Rhodia	F	102	1.8
Borealis	AD/Au	110	1.7
DIC	J	132	1.6
Air Products	US	116	1.5
Celanese	D	75	1.5
Praxair	US	74	0.8
Linde	D	92	0.7
LyondellBasell	NL	145	0.7
Chevron-Phillips	US	38	0.5
Braskem	Brazil	29	0.4
Yara	Nor	14	0.1

Note: AD/Au = Abu Dhabi/Austria, B = Belgium, CH = Switzerland, D = Germany, F = France, J = Japan, NL = Netherlands, Nor = Norway, US = United States.

Source: Chem. Eng. News, 26 July 2010.

research related to finding new materials for which uses could be created. Thus the period between 1930 and 1965 was a time of great discovery. The polymers that provide plastics, synthetic fibers, elastomers, coatings, and adhesives are examples. Chemicals were also discovered with numerous applications that made industry generally more efficient, such as corrosion inhibitors, electronics chemicals, and food antioxidants.

In the mid-1960s, however, the concept changed to “demand pull.” What problems are there in the marketplace that require technical solutions? Market research to answer such questions became a discipline and, for the past 45 years, the industry

TABLE 1.9 Top 40 United States Chemical Companies

Rank	Company	Headquarters Country	Chemical Sales (\$ million)	Chemical Operating Profit as % Chemical Sales	Chemical Sales as % Total Sales
1	BASF	D	54,817	3.5	77.6
2	Dow Chemical	US	44,875	3.9	100
3	Sinopec	RC	31,302	6.4	15.9
4	INEOS Group	CH	28,600	n.a.	100
5	ExxonMobil	US	26,847	8.6	8.9
6	DuPont	US	25,960	9.5	99.4
7	Formosa Plastics Group	TwN	25,437	6.5	61.9
8	Royal Dutch/Shell	NL	24,586	n.a.	8.8
9	Sabir	SA	23,096	25.6	84.0
10	Total	F	20,521	3.8	11.2
11	LyondellBasell	NL	19,993	3.1	64.9
12	Bayer	D	19,551	3.8	45.0
13	AkzoNobel	NL	19,360	5.9	100
14	Mitsubishi Chemical	J	16,742	def	62.4
15	Air Liquide	F	15,303	n.a.	91.7
16	Evonik	D	14,030	15.9	77
17	Sumitomo Chemical	J	13,121	1.8	75.8
18	Mitsui Chemicals	J	12,892	def	100
19	LG Chem	SK	12,625	13.9	100
20	Toray Industries	J	12,450	2.8	85.8
21	Linde	D	12,447	26.6	79.7
22	Reliance	IND	12,240	14.6	27.9
23	PPG Industries	US	11,390	10.8	93.1
24	DSM	NL	10,962	13.7	100
25	Mosaic	US	10,298	23.7	100
26	Shin-Etsu Chemical	J	9782	12.8	100
27	Yara	Nwy	9763	12.1	100
28	Asahi Kasei	J	9452	3.5	61.8
29	Praxair	US	8956	30.8	100
30	Sasol	SAf	8954	def	54.6
31	Syngenta	CH	8420	22.9	76.6
32	Chevron-Phillips	US	8406	8.4	100
33	DIC	J	8090	3.7	100
34	Solvay	B	7935	5.9	67.1
35	Air Products	US	7766	15	94.1
36	Huntsman Corporation	US	7763	0.8	100
37	Braskem	Br	7633	9.2	100
38	Lanxess	G	7047	4.6	100
39	Tosoh	J	6711	2.1	100
40	Borealis	Aus	6569		100
41	Arkema	F	6193		100

TABLE 1.9 (Continued)

Rank	Company	Headquarters Country	Chemical Sales (\$ million)	Chemical Operating Profit as % Chemical Sales	Chemical Sales as % Total Sales
42	Clariant	CH	6090	3.7	100
43	Rhodia	F	5617	5.4	100
44	ENI	I	5525	def	4.8
45	Showa Denko	J	5489	0.4	75.8
46	Merck KGaA	D	5348	18.1	52.0
47	Dow Corning	US	5093	n.a.	100
48	Celanese	US	5082	9.0	100
49	Eastman Chemical	US	5047	10.2	100
50	Hitachi Chemical	J	4860	8.4	100

Note: Aus = Austria, B = Belgium, Br = Brazil, CH = Switzerland, RC = China, D = Germany, F = France, IND = India, I = Italy, J = Japan NL = Netherlands, Nwy = Norway SA = Saudi Arabia, SAF = South Africa, Twn = Taiwan, UK = United Kingdom, US = United States.

has talked of “market orientation.” Examples of technology push include television, lasers, and dendrimers (Section 17.4.4). Examples of demand pull include hard-water-compatible detergents, jumbo jets, and automobiles with low exhaust emission.

The isomerization of *m*-xylene to *p*-xylene (Section 4.8) is an obvious example of a market-oriented research project. Catalytic reforming gives a mixture of xylenes containing too much *m*-xylene for the market and too little *p*-xylene for conversion to terephthalic acid for polyester production (Table 4.10). Were sufficient *p*-xylene produced to satisfy the market, there would be a huge excess of the other isomers. Originally, a catalyst was developed that would isomerize the residual xylene mixture left after the *p*-xylene had been separated, and *p*-xylene was then separated again by the tedious process described in Chapter 11, and the residual mixture isomerized and recycled again. But the fast-growing demand from China and East Asia for polyester fabrics led to market pressures that were satisfied by the development of a further process based on surplus toluene. A conventional acid catalyst will disproportionate this to benzene and a mixture of xylenes, which have to be separated as before. With a zeolite catalyst, however, the major xylene obtained is the *p*-isomer. Section 10.1 describes this sophisticated market-oriented chemistry.

Both “technology push” and “demand pull” should be part of any large company’s research plan, although there has been a marked trend to deemphasize the “blue skies” research that leads to truly novel discoveries. Thus first generation research was “blue skies” research. It required little participation by management, and researchers were generally regarded as a group of people difficult to communicate with. It was only when a project reached the development and marketing stages that management was required. DuPont, General Motors, and IBM are examples of companies that made discoveries and brought them to the marketplace. Second generation research

involved going to the marketplace to find out what was needed. This demanded strong participation on the part of the marketing branch, but still little participation by top management.

Today there is a third generation of research managers who recognize that research should be a part of the organization not apart from it. R&D should figure in corporate objectives and should take its direction from these objectives in exactly the same way as any other business function. It should thus help the organization to achieve its overall goal. Indeed it should even help to set goals by managing technology as opposed only to inventing and applying it.

Thus the R&D department must determine which technologies may be developed internally, which may be obtained through licensing, and which may be obtained through strategic alliances. This is very much like a "make-or-buy" decision in manufacturing. It was obviously better for many companies to license BP's ammoxidation technology (Section 6.5) than to try to work out an acrylonitrile process on their own. Today well over 90% of all acrylonitrile is made by this process. Similarly, Himont developed highly sophisticated catalysts for propylene polymerization, and then joined forces with Mitsui. Both companies had strong backgrounds in catalyst development, and jointly they could bring these to bear on their objectives.

Metallocene catalysts (Section 17.3.12) make possible the synthesis of polymers previously difficult to obtain by Ziegler-Natta catalysis. One example is syndiotactic polystyrene, a high melting specialty or engineering polymer. Both Dow and Idemitsu developed this polymer but, instead of carrying out competing research and development programs, the companies joined forces. Once the project had passed the pilot plant stage, they parted company, and each pursued its own commercial strategy.

A sensible R&D strategy avoids duplication but, even so, a large amount of duplication takes place in the world's research laboratories. The patent literature discloses 25 processes for the manufacture of 1,4-butanediol and a similar number for manufacture of propylene oxide. At least 15 companies have worked on the homologation of methanol to higher alcohols, a process that none has commercialized. There are many other examples.

There is also duplication in the competition between companies in the specialty and performance polymers business. Not only is there intercompany competition to sell the same polymer but there is also much interpolymer competition as different polymers vie for use in a given application. In 1993 there were at least 51 companies manufacturing engineering thermoplastic polymers, that is, sophisticated polymers to replace metal. Sixty percent of the business was enjoyed by only five companies: General Electric, DuPont, Bayer, Hoechst Celanese, and BASF. Another eight companies had 19% of the business; these were Allied, Monsanto, Asahi Chemical, Mitsubishi Gas Chemical, Teijin Seiki, Mitsubishi Chemical, DSM, and Toray. The remaining 21% of the business was the province of 37 companies, none of which had achieved the critical mass required for profitability in the engineering polymer business. On the one hand, this kind of operation leads to a great deal of waste. On the other hand, it may be the concomitant of a competitive capitalist economy.

Experience in centrally planned economies, especially in pharmaceuticals research, suggests that without the spur of competition very little is discovered. Having a

number of groups trying to get something to work will at least increase the possibility that one of them will succeed.

Of the \$37 billion spent on chemical and drug industry research in 2009, about 10% was for basic research, 35% for applied research, and 55% for development. There has always been an academic argument that holds that basic research is the province of the university. This may well be so, but in any laboratory there may be need for theory that has not been developed but is necessary for the solution of a problem. The pursuit of this theory, which in essence is basic research, is appropriate for the industry that requires it in order to fulfill its objectives. This leads to many industry–academic collaborations and to industrially funded research in universities.

Applied research is usually defined as the type of R&D that leads to new uses for existing products or new products that fill needs in the marketplace. The development of a new polymer that absorbs many times its weight of water for use in disposable diapers is a good example of applied research, as is the extension of the use of that material to other areas such as agriculture. All the same, very little effort is being expended on new products. One reason for this is that the maturity of the industry does not offer as many opportunities for them. Also, the many regulations that govern the chemical industry, particularly the Toxic Substances Control Act (Section 1.3.4) and the REACH regulations, require extensive and expensive testing before a product can be test-marketed. Usually the risk is deemed greater than the potential benefit. A major exception is found in the pharmaceutical and agricultural chemical businesses. In the 2000s it cost approximately \$500–1000 million to develop a new pharmaceutical. The pharmaceutical companies have traditionally been willing to make such expenditures because of the lure of “blockbuster” drugs whose annual sales may exceed a billion dollars with concomitant profits. Today even this business model is being questioned.

The bulk of R&D dollars is spent on applied research and development. This includes work on new and improved processes, finding new uses for existing products, pursuing the analytical activities on which a modern laboratory depends, and solving ecological problems.

Ecological problems – the monitoring and reducing of pollution – have become a major research area in the past generation. One-fifth of new capital expenditures in the 1990s was said to be for pollution abatement and control; approximately the same amount of the R&D budget of a large company is likely to be spent on ecologically oriented projects.⁹

While patent applications are not an infallible sign of innovative activity, it is perhaps significant to note that, between 2000 and 2010, patent applications in China rose sevenfold from 55,000 to 380,000, compared with Japan (425,000 dropping to 345,000) and the United States (275,000 rising to 450,000).¹⁰

1.3.6 Dislocations

An important concept in today’s chemical industry is the ever-present possibility for dislocations. This applies all too often to planners, who find their scenarios askew because of a dislocation. Dislocations are defined as events over which a given

company has no control but which markedly affect that company's business. In planning, one cannot forecast what a dislocation might be. Indeed, if it could be forecast, it would not be a dislocation. But what must be anticipated in planning is that there will be dislocations either for good or ill.

A few examples illustrate the point. The advent of unleaded gasoline made lead tetraalkyls obsolete in the United States. The major manufacturer of these compounds was Ethyl Corp. with a reputed \$90 million of profit. That figure rapidly declined to \$20 billion and would have been lower had it not been for export sales. Obviously, Ethyl was a victim of a dislocation. That motivated Ethyl to use its skills to expand into a variety of specialized and semicommodity businesses that allowed them to recoup their profits. Thus they became a large supplier of the bulk pharmaceutical, ibuprofen, for sale to packagers, who converted it into a consumer item. Their synthesis involved organometallic chemistry developed for the unrelated area of both lead tetraethyl and α -olefin production.

The same unleaded gasoline dislocation proved to be a windfall for ARCO. ARCO's two-for-one process for the manufacture of propylene oxide and *t*-butanol (Section 4.7) made available to them large quantities of the latter for which, at the time the plant went on stream, there was very little use. Accordingly the *t*-butanol was recycled to the starting material, isobutene. The need for octane improvers in unleaded gasoline soon provided a market for it. Dehydration to isobutene and reaction with methanol provided MTBE (Section 4.15.1) and ARCO became the largest single supplier in the United States. Between 1977 and 1993, production rose from virtually nil to about 13 billion pounds per year and had reached 20 billion pounds by the end of the 1990s. Capital expenditure was conservatively estimated at \$50 billion. There was then another dislocation. Although MTBE functions well as an octane improver, it is water soluble. If there is a leak from a gasoline storage tank in a garage, the MTBE diffuses into the groundwater. Gasoline, which is insoluble, does not give this problem. Inspection and repair of hundreds of thousands of gasoline storage tanks was judged impracticable, and instead ethanol was proposed as a replacement for MTBE. The ethanol is made mainly by fermentation of corn starch and this requires subsidy (Section 5.9).

A third example also relates to unleaded gasoline. At least one petroleum company announced that it would achieve the desired octane number by removing lead and increasing the aromatics content of its gasoline. A few years later, the Clean Air Act specified that the aromatics content of gasoline must be decreased from about 35% to 25%. Thus the Clean Air Act provided a second dislocation that negated that company's reaction to the earlier dislocation provided by unleaded gasoline.

A fourth example: Phillips Petroleum Company never used the metathesis reaction (Section 4.14) to convert propylene into ethylene, which was more expensive at that time, and 2-butene which, in turn, could have been dehydrogenated to butadiene. One might assume that it did not opt to carry out this interesting chemistry because of the widely held belief in the 1970s that within a 15-year period declining U.S. gas supplies would make naphtha and gas oil the major steam cracking feeds. Accordingly, large quantities of butadiene would become available. The United States has always imported butadiene from Europe because insufficient quantities were produced by

the cracking of gas. Actually naphtha and gas oil never became major feedstocks in the U.S. chemical business (Section 4.5.1). Saudi Arabia decided to use only the ethane in their associated gas, making large quantities of LPG (propane and butane) available at low world prices. The United States now uses LPG to supplement indigenous ethane and propane and has not found it necessary to switch to liquid feeds. Thus the United States still imports butadiene, a situation that metathesis might have helped to avoid. In a related dislocation, recent advances in the recovery of shale gas (Section 4.2) have meant that the \$1.5 billion LNG terminal at the Sabine Pass on the Texas–Louisiana border was largely unused when it first became available.

Dislocations frequently result from advances in technology. The producers of propylene oxide by the chlorohydrin route suffered a serious dislocation when ARCO announced its new process via *t*-butyl hydroperoxide (Section 6.8). Every manufacturer except one went out of business. Similarly Monsanto's acetic acid process using methanol and CO closed down every U.S. producer of acetic acid who used acetaldehyde as a starting material.

World events are also dislocations. Booms and slumps, sudden changes in the price of oil or natural gas, political upheavals such as the 9/11 destruction of the twin towers, and the Iraq and Afghan wars all influence the general economic climate and the chemical industry. The rupture of BP's oil well in the Gulf of Mexico in 2010; the Japanese earthquake, tsunami, and destroyed Fukushima nuclear plant in March 2011; the "Arab Spring" and the death of Osama bin Laden are all expected to have far-reaching effects although no one knows what they will be.

The answer to dislocations is the concept of robustness. A robust process is one that can accommodate a variety of dislocations. For example, some companies, uncertain of their feedstock supply, built steam crackers that could operate on gaseous or liquid feedstocks. Their plants cost more than a single feedstock plant would have cost, but were sufficiently robust to withstand dislocations in feedstock supply. The fact that the petrochemical business in the United States in 1993 remained relatively profitable was due largely to such flexible crackers. Western Europe suffered because only five of its 52 crackers at that time were flexible. This was originally dictated by the lack of availability of gas.

Finally, the chemical business is dynamic. It is affected not only by what it does itself, such as creating new technology, but by what others do around it. Modern managers keep abreast as much as possible with what the rest of the world is doing that might affect their businesses. The development of desk-top computers, the World Wide Web, and specialized databases have provided rapid access to previously undreamed of amounts of information about companies, patents, products, and applications.

1.4 THE TOP COMPANIES

In 1970, of the 50 largest chemical companies in the world, 23 came from the United States, 19 from Western Europe, and 8 from Japan. Of the top 250 companies, only seven came from what we would call developing countries (four in India and three in

Mexico). Countries with 30% of the world's population produced 90% of the chemicals. This dominance is now being eroded, and details of the changes will be discussed in the next chapter.

Meanwhile, the United States is still the largest and most important chemicals producer, and the top 40 U.S. companies are listed in Table 1.9. The year 2009 was bad for chemical companies and the top 50 companies combined suffered a 21% decline in sales compared with the previous year. While there are hopes for an upturn in 2010, the 2009 list still shows the pattern of the U.S. industry.

The industry is dominated by a handful of very large companies. The sales of the top 50 companies were \$247.5 million and the top company, Dow, accounted for almost one-fifth of this. The sixth ranked company had only a fifth of the sales of the top ranked company. From our point of view, the companies may be subdivided. Some, such as Dow, DuPont, and Chevron Phillips, are integrated chemical companies making downstream products, but not themselves involved with the petroleum industry. Praxair and Air Products make industrial gases. Mosaic is the highest ranked inorganics company making nitrogen–phosphorus–potassium (NPK) fertilizers and animal feed. ExxonMobil and Occidental Petroleum are oil companies that have expanded downstream. Huntsman is a private equity conglomerate (Section 2.2.2). Dow Corning makes silicon compounds. The large volume inorganics are exemplified by fertilizers and these sell for low prices.

1.5 THE TOP CHEMICALS

Table 1.10 lists the 48 most important chemicals by volume manufactured in the United States in 2000 and 2008. The rank order would be more or less the same in any developed country.

Sulfuric acid heads the list by a large margin as befits its position as an economic indicator, although its maturity means that its growth has been slow. Though it has many applications, about 45% is used for phosphate and ammonium sulfate fertilizers. Of the first ten chemicals only three—ethylene, propylene and ethanol—are organic, and ethanol only ranks because of its fuel use and was produced in far smaller quantities in 2000. Four large tonnage chemicals are associated with the fertilizer industry—sulfuric acid, nitrogen, ammonia, and phosphoric acid. Oxygen is used by the steel industry and for welding. Sodium carbonate is important in the glass industry. Most of these chemicals are also used to make organic chemicals, but their main markets lie elsewhere. Chlorine has a number of uses including the bleaching of paper, as a disinfectant, and as a component of organic compounds, most important of which is vinyl chloride whose precursor is ethylene dichloride. Many chlorine compounds, however, are now considered ecologically undesirable, as is the use of chlorine for bleaching paper and disinfecting swimming pools.

The three most important organic chemical building blocks—ethylene, propylene and benzene—occupy positions 4, 6, and 16. The majority of remaining chemicals in the top 48 are organic, and these form the backbone of the so-called heavy organic

TABLE 1.10 Top Inorganic and Organic Chemicals and Fertilizers, United States 2008

Product Description	2000 (thousand metric tons)	2008 (thousand metric tons)
Sulfuric acid, gross (100%)	39594	32381
Nitrogen	28478	NA
Oxygen	25679	NA
Ethylene	25113	22554
Lime	20104	NA
Propylene	14457	14783
Chlorine gas	14000	10669
Ammonia, synthetic anhydrous	14342	9571
Phosphoric acid (100% P ₂ O ₅)	11333	9216
Sodium carbonate	10247	NA
Ethylene dichloride	9911	8973
Sodium hydroxide, total liquid ^a	11523	8111
Vinyl chloride	8596	7782
Nitric acid (100%)	7900	7245
Ammonium nitrate, original solution	7239	7114
Benzene	8045	5588
Ethylbenzene	5967	4104
Styrene	5405	4100
Superphosphates and other fertilizers (100%P ₂ O ₅)	8073	5539
Urea (100%)	6969	5241
Hydrochloric acid ^b	4717	3902
Cumene	3741	3386
Ethylene Oxide	3867	2903
Ammonium sulfate	2548	2514
Phenol	2200	1990
1,3-Butadiene	2009	1633
Vinyl Acetate	794	1267
Sodium silicates ^c	1136	1106
Acrylonitrile	1551	1018
Aniline	846	1009
Aluminum sulfate (commercial) ^d	1076	NA
Finished sodium bicarbonate	536	682
Sodium chlorate	940	607
Potassium hydroxide liquid ^a	539	582
Hydrogen peroxide	1083	437

^a Liquid production figures represent total production, including quantities later evaporated to solid caustic.

^b Includes production from salt and acid.

^c Excludes amounts produced and consumed in making meta, ortho, and sesquisilicates.

^d Excludes quantities produced and consumed in municipalities.

Source: U.S. Census Bureau, Current Industrial Reports, "Inorganic Chemicals," Series MQ325A, and "Fertilizers and Related Chemicals," Series MQ325B.

chemical industry. Heavy organics are defined as large volume commodity chemicals such as ethylene and propylene as opposed to specialty chemicals such as dyes and pharmaceuticals. Some of the chemicals have only one very large use. For example, the major use for ethylene dichloride (#11) is to make vinyl chloride (#13). The major use for ethylbenzene (#17) is to make styrene (#18). Cumene (#22) is converted to phenol (#25).

Many of the top chemicals are monomers for polymers, including ethylene, propylene, vinyl chloride, styrene, terephthalic acid, formaldehyde, ethylene oxide, ethylene glycol, phenol, butadiene, propylene oxide, acrylonitrile, vinyl acetate, adipic acid, and caprolactam.

In 2000 we noted that the composition of the list of top chemicals had remained fairly steady over the years, and this still applies, although methyl-*t*-butyl ether is a notable dropout and has been replaced by fermentation ethanol.

Comparison of the 2008 data with the 2000 data shows the maturity of the chemical industry, indeed the decline in the U.S. industry. If one takes the recession year of 2009, the decline is much greater, but there is hope that 2009 was a one-off. A noteworthy change is a decrease in the ethylene/propylene ratio, and this will be discussed in the following chapter.

ENDNOTES

1. http://factfinder.census.gov/servlet/SAFFEconFacts?_sse=on&_submenuId=business_1.
2. Labor costs vary depending on whether they are direct costs or involve the maintenance staff, security staff, sales staff, and so on. The lowest figure we have seen allowed labor as 0.5% of total costs on an ethylene cracker. The BP/ICI olefins 6 cracker at Wilton, Teesside, UK (now purchased by Huntsman) employed fewer than one hundred people in the mid-1970s, all pictured in *Cracker*, ICI Schools Liaison Section, Welwyn, 1980. As one moves further downstream from ethylene, the proportion of costs attributable to labor rises.
3. T. Hartung and C. Rovida, Chemical regulators have overreached. Opinion, *Nature*, vol. 460, 27 August 2009; ECHA — New study inaccurate on the number of test animals for REACH, Helsinki, 28 August 2009.
4. The differences between the United States and Western Europe regarding chemicals registration are discussed in *Chem. Eng. News*, 11 February 2008.
5. See for example, C. F. Cranor, *Legally Poisoned*, Cambridge MA: Harvard University Press, 2011.
6. B. G. Reuben, *Chem. Ind.* in press.
7. C. Everett Koop's attack on phony chemical scares appeared in the *Wall Street Journal*, 22 June 1999 and there was a counterblast at www.mindfully.org.pesticide.
8. Based on B. T. Mossman et al., *Science*, 19 January 1990; see also <http://spiderjohnson.com/asbestos.html>.
9. Data on the chemical industry and its contribution to pollution abatement can be obtained from the American Chemistry Council, Government Relations Department, Washington DC. The CMA indicated in a bulletin issued in 1992 that pollution from the chemical

industry had decreased 60% and that the industry in 1990 had spent \$3.8 billion on pollution abatement. This was five times the 1975 level. Cost for pollution abatement in the year 2005 in 1990 constant dollars is estimated to be \$11 billion, mostly as a result of the Clean Air Act. In the early 1990s about 20% of all capital investment of the industry was directed toward pollution abatement and pollution control.

10. *London Times*, 21 January 2011, p. 42.

CHAPTER 2

Globalization of the Chemical Industry

Maturity, highly prized in an individual, is feared in an industry. This chapter deals with the maturing of the chemical industry in three developed countries (the United States, Western Europe, and Japan) and the resultant restructuring, mergers, and acquisitions. It considers the importance of international trade to the industry, and the emerging competition from developing countries. The shipping of chemicals around the world has increased and, as it adds about 10% to their cost, we shall discuss the technology of chemicals shipping in Chapter 3.

When we wrote about the chemical industry in 1980, we explained that the organic chemicals industry was dominated by the United States, which cracked ethane from natural gas, Western Europe, which cracked naphtha from refineries, and Japan, which cracked imported naphtha. We also stressed its growth. Between 1954 and 1974 the U.S. chemical industry grew at a rate of 8.5–9%. Between 1964 and 1974 the Japanese industry grew at a rate of 11.7%. Western Europe during that period enjoyed a 9.7% growth. In 1976 the U.S. industry, coming out of a recession, grew 17%, although this included 5–8% of inflation. We pointed out that inevitably growth must lessen and that the industry would eventually grow at the rate of the economy as a whole. We also pointed out that government regulations relative to pollution, worker safety, and ecology generally would take its toll on profitability. By the early 1990s all of this had come to pass. The industry had matured. No company could operate in the chemical industry unless it understood fully all the ramifications of maturity, which expresses itself in overcapacity, intense competition, low prices, and low profitability.

Ultimately it leads to restructuring which, between 1980 and 1999 involved an estimated \$5.25 trillion of assets—a figure that has probably doubled since then. All of these things have happened in the chemical industry not only with commodity chemicals, the ones we are mainly concerned with in this volume, but also with specialties.

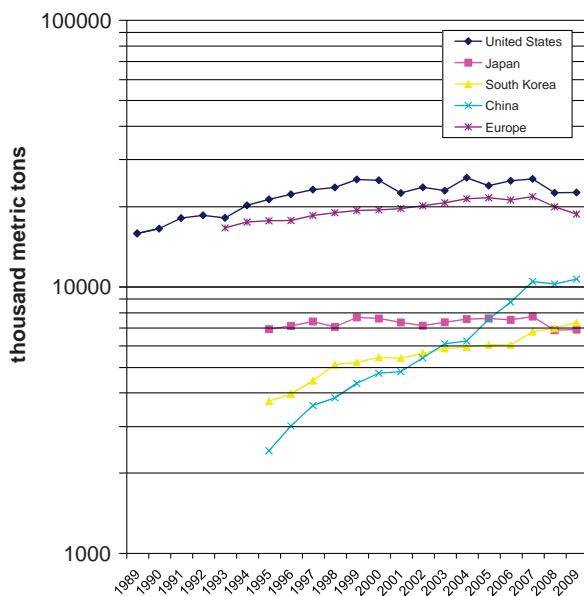


FIGURE 2.1 Ethylene production in five regions.

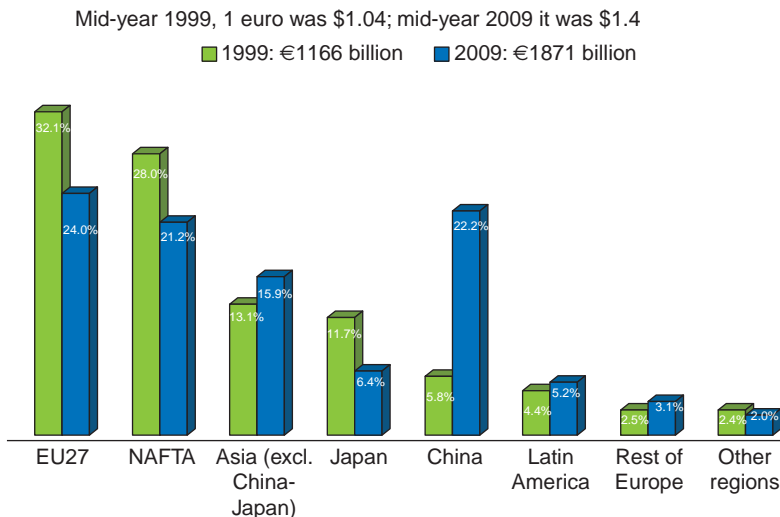
Maturity occurs because of market saturation, wide diffusion of technology, and low barriers to entry to the industry. Engineering companies are eager to build turnkey plants and train clients to operate them, which encourages overproduction. Maturity is hastened by competition from developing countries, especially those with indigenous sources of petroleum and natural gas and whose governments are anxious to industrialize even if the emergent industries need to be subsidized. These issues are discussed below.

For the years 1989–2009 maturity is demonstrated in another way. The standard measures of inter-country comparison are unreliable because of inclusion or exclusion of pharmaceuticals, changes in exchange rate, and so on. Instead, we have taken ethylene production as a surrogate for activity in the organic chemicals industry, and Figure 2.1 is a logarithmic plot of data for five regions.

Over a 16-year period (1995–2009), ethylene production in the United States and Europe increased by only 0.4% per year and Japanese production actually decreased. South Korean production, on the other hand increased by 4.3% per year and Chinese by 9.7% per year.

These growth rates take their toll of market share. Figure 2.2 shows world chemical sales by region between 1999 and 2009.

The developing countries of Asia are expanding their production of chemicals at a rapid rate. The developed world, while still a long way ahead, is essentially static. The motives of the developing world are partly to use indigenous raw materials, previously exported to the developed world, partly to modernize their societies, and partly to supply local markets. The aim of supplying to local markets applies to Southeast Asian countries. In the Middle East, local markets are small and production is largely



Source: Cefic Chemdata International

FIGURE 2.2 World chemical sales by region, 1999–2009. (1) Includes China, India, South Korea, Thailand, Taiwan, Indonesia, Malaysia, and Singapore but not Japan. (2) NAFTA = United States, Canada, and Mexico. (Source: CEFIC Chemdata International.)

exported. The oil-rich governments are diversifying downstream. Many of the new plants are state sponsored and frequently subsidized. Profit is not necessarily the prime motive and the production in these countries contributes to the chronic chemical industry problem of overcapacity.

2.1 OVERCAPACITY

Restructuring is the inevitable result of overcapacity and is well demonstrated with ethylene. By the late 1970s the capacity for ethylene manufacture far exceeded the demand. Restructuring started in 1986 and first of all involved reduction in personnel. The chemical industry in the United States employed about 1.15 million people. This number was cut by 7–8% by attrition, early retirement, and redundancy. Second and most important was reduction in productive capacity to bring it in line with demand.

Figure 2.3 shows what happened relative to U.S. demand versus capacity for ethylene. Capacity in 1981 was about 18 million metric tons. By 1986 this had decreased to about 16 million metric tons. This 10% cut in capacity coupled with growth in ethylene usage brought demand and production into line by 1987. The growth can be attributed first of all to stockpiling of downstream products—ethylene itself cannot be stockpiled—since companies tend to amass materials when a shortage appears imminent, for example, when capacity is being eliminated. But also, when business improves, companies are more prone to invest in new applications and to expand old ones, and this reflected itself in growth for the polyethylenes, which in turn resulted in growth of ethylene. Thus the period encompassing 1987 and 1988 was

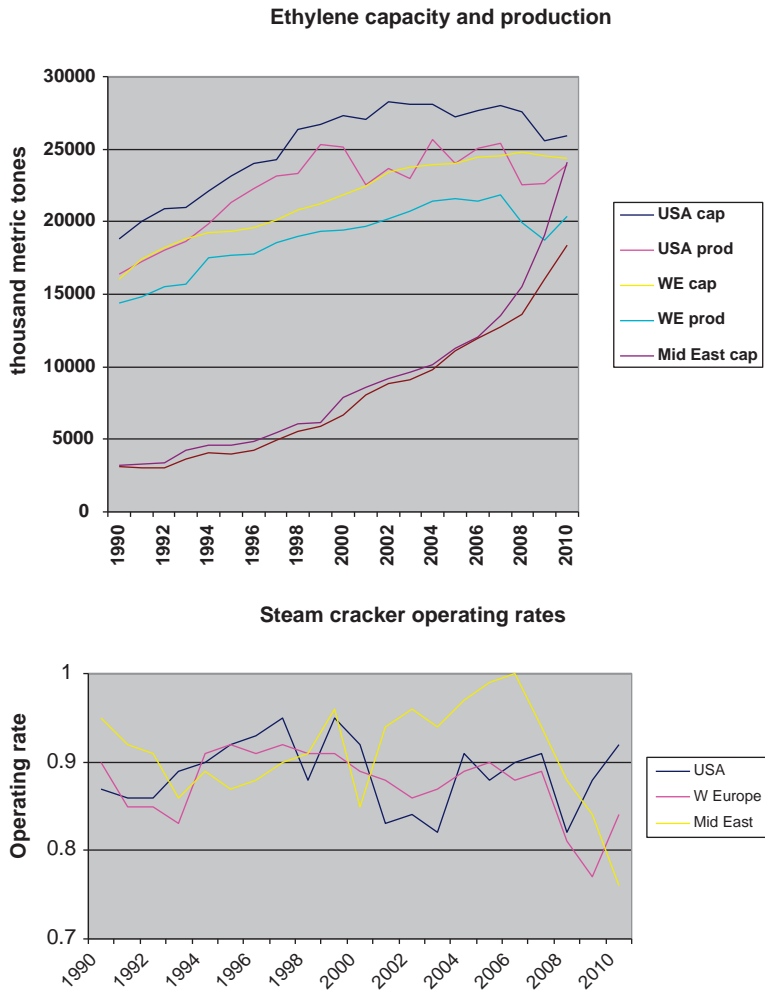


FIGURE 2.3 Ethylene capacity, production, and operating rates. USA = United States, WE = Western Europe, Mid East = Middle East, cap = capacity, prod = production. (Source: Nexant Inc.)

probably the most profitable the chemical industry in the United States has ever enjoyed, the value of shipments between 1987 and 1989 in real terms increasing 8.6%. But the honeymoon was over by 1989 for the industry started to debottleneck existing plants and to build new capacity. By 1991 there was again appreciable overcapacity and need for further restructuring. The late 1990s saw a boom again, followed by a trough in 2000, and a boom again roundabout 2006.

Western European capacity and demand were similarly in balance in 1989/1990, as shown in Figure 2.3, but the construction of new crackers by Fina, Veba, BP and BP

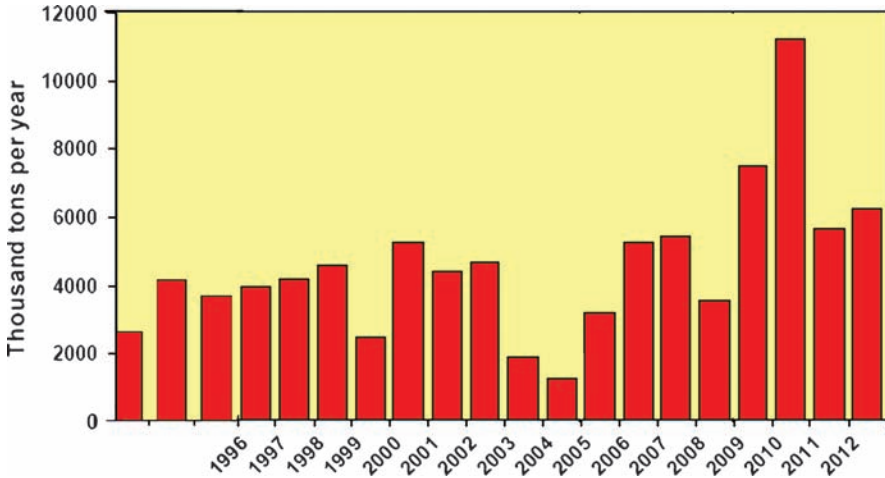


FIGURE 2.4 Annual addition to global ethylene capacity. (Source: Nexant Inc.)

with ENI, BASF, and Hüls opened up a large gap by 1993/1994. Average European operating rate was down to about 83% of nameplate capacity and at the time of writing no new European cracker has since been built. The operating rate limped along at about 92% in the late 1990s, with strong ethylene demand growth of the order of 5% per year. The downturn after 2007 was especially marked with crackers that were operating at about 80% of capacity. Meanwhile, huge new capacity was being added in developing countries (Fig. 2.4). Six newer players — Reliance Industries of India, NPC Iran, Formosa Plastics, Sinopec, Sasol, and SABIC—brought on stream capacity they had planned in the brighter days at the beginning of the decade. Less than 2 million metric tons per year capacity was added in 2003 and 2004 but after that the industry threw caution to the winds. Figure 2.4 shows the annual additions to capacity. Figure 2.5 shows the situation as it was in 2007. At that time, the installed capacity in the Middle East was about 13 million metric tons/year and by 2010 it had doubled. The main producers are Saudi Arabia with about half the Middle East capacity and Iran with a quarter. Qatar, Abu Dhabi, Kuwait, Oman, and Egypt are also involved but on a much smaller scale. Meanwhile, China, which does not have indigenous petroleum supplies, doubled its ethylene capacity from 6 to 12 million metric tons/year over the period 2002–2010.

It is difficult to see how these capacity increases can be absorbed, and it is rumored that some of the older European crackers may be closed. Furthermore, the overcapacity situation is likely to be exacerbated by the development of shale gas (Section 4.2). The building of crackers in the United States and Europe has been inhibited by depletion of gas reserves and the high cost of feedstocks. Early in 2011, American companies were rushing to announce plans to capitalize on the perceived shale gas bonanza. Dow, for example, plans to build a world-scale cracker on the U.S. Gulf Coast for start-up in 2017, based on gas from the Marcellus and Eagle Ford shale regions. It has other less ambitious plans for other ethylene plants at St. Charles, near

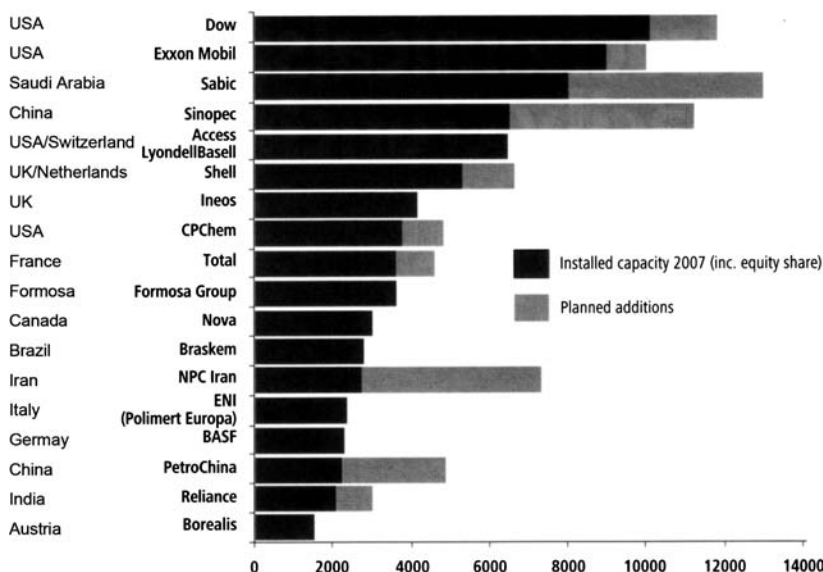


FIGURE 2.5 Global ethylene capacity (thousand metric tons/year). (Source: A. McRae, *Chem. Ind.* 29 September 2008, 16–20.)

Hahnville, Louisiana (end of 2012), Plaquemine, Louisiana, in 2014, and Texas in 2016,¹ leading to a capacity increase of 30%. Bayer has expressed willingness to host an ethylene cracker at one of its sites at West Virginia, which sits on the Marcellus formation. Shell Chemicals, Chevron-Phillips, LyondellBasell, and especially ExxonMobil are also showing interest. The last of these claims credit in TV advertisements for shale gas development. Thus the world is likely to be awash with ethylene for the foreseeable future.

The chemical industry, certainly since 1970, has been cyclical. A strong market leads to overbuilding of plants that come on stream at the wrong time. This leads to overcapacity. There is then intense competition with subsequent low prices and low profitability. With the average return on sales approaching zero, the less efficient producers are forced out of the market, which then rises again. Prices are depressed until growth of demand or closure of plants takes up the spare capacity. As illustrated in Figure 2.6, there have been repeated cycles with minima in 1982, 1993, and 2002. This pattern is referred to as “the old paradigm.”

Compared with other industries, the chronic overcapacity of the chemical industry is related to its being capital intensive with high fixed and low variable costs. There is a large gap between the break-even price of products (when price equals total cost) and the price at which it is rational to shut down a plant (when price falls below cash cost — see Appendix A). Furthermore, because of economies of scale, it may be more economic to run a plant at full capacity even if it means cutting prices. Finally, third world countries see a chemical industry as an acceptable way to industrialize, and some of them, for example, Malaysia, Saudi Arabia, and Venezuela, have access to

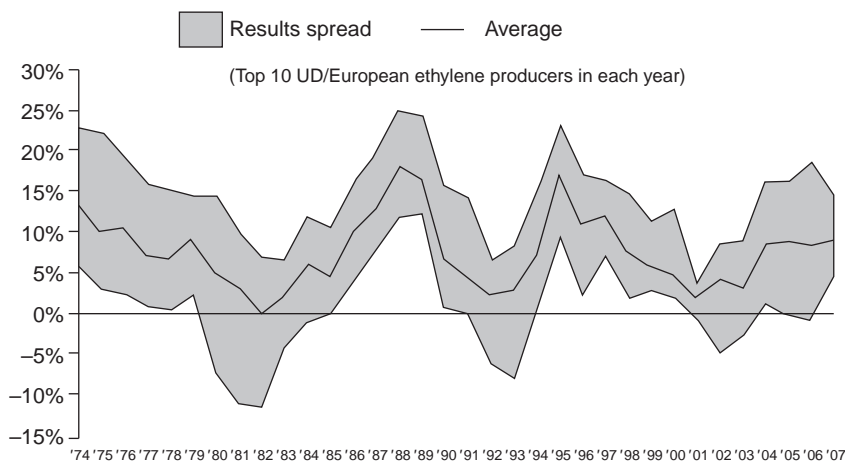


FIGURE 2.6 Return on sales of major ethylene producers over time. (Source: A. McRae, *Chem. Ind.* 29 September 2008, 16–20.)

cheap indigenous supplies of oil and natural gas. Thus the chemical industry is always inclined to “shoot itself in the foot.”

2.1.1 Economic Cycles

Another problem that exacerbates overcapacity is that the chemical industry participates in the economic cycles (boom and bust) that are part of a capitalist economy. A rise in demand by consumers leads to higher prices and rising profitability in industry. That prompts additional investment to satisfy the demand, and the extra money pumped into the economy fuels further rises in demand. This is the “boom” stage of the cycle. Because building new plants takes time, the increase in supply lags behind the rise in demand. Thus there is usually an overinvestment and the increase in supply causes prices and profits to fall. Investment is cut back, plants are closed (rationalization!), workers are made redundant, and the drop in demand is accelerated. This is the “bust” stage of the cycle and it continues until the overshoot in plant closures leads to an excess of demand once more. The widely quoted figure for length of cycle is 4–5 years from slump through recovery, boom and recession again; but the data for return on sales of ethylene show intervals of 9, 7, and 11 years between peaks. Thus we may hope for another peak around 2017.

The question for the chemical industry is how to invest the large amount of money made during the boom years, especially as the time taken to build plants means that facilities built at the top of the cycle will come on stream during its decline.

Investment in areas outside the chemical industry has been tried with mixed results as has a company buying back its own shares to reduce its equity base. The drawback is that their price at the top of the cycle will be high. Nonetheless, Wall Street frowns on accumulating cash, so there is pressure to invest in new facilities. Also, cash makes the company a target for takeover.

The markedly increased profitability (a “fly-up”) in 1994/1995 was caused by accidents in plants all over the world. Three crackers in the United States blew up. In Europe and Southeast Asia there were similar disruptions. This created a shortage, remembering that a shortage in the chemical business is only a 2–3% shortfall. Plants were soon repaired and the fly-up was over. In 2001 there was a decrease in profitability largely because of the expensive gas (10 cents per BTU in January) and cheap imports. The higher oil and gas prices could not be passed on to the consumer because of competition resulting from overcapacity.

2.2 RESTRUCTURING, MERGERS, AND ACQUISITIONS

Over the past 18 years, the world chemical industry has undergone considerable, one might almost say dramatic, restructuring. The leading companies have changed, as have their portfolios. Table 2.1 shows the 20 leading chemical companies in 1970, 1990, and 2009, and Table 2.2 gives the 2009 top-50 list with some financial information. Pharmaceutical companies have been excluded unless they have extensive chemical interests. Some of these chemical companies have nonchemical activities and the proportion of chemical sales is shown in the final column.

TABLE 2.1 Top Chemical Companies,^a 1970–2009

1970		1990		2009	
Du Pont	US	BASF	D	BASF	D
ICI	UK	Hoechst	D	Dow	US
Union Carbide	US	ICI	UK	Sinopec	RC
Hoechst	D	Bayer	D	INEOS	CH
BASF	D	Du Pont	US	ExxonMobil 1	US
Montecatini-Edison	I	Dow	US	Du Pont	US
Bayer	D	Exxon	US	Formosa	TwN
Akzo	NL	Shell	NL	Shell	NL
Rhone-Poulenc	F	Rhone Poulenc	F	SABIC	SA
Monsanto	US	Ciba	CH	Total	F
Grace W.R.	US	Eni	I	LyondellBasell	NL
Dow	US	Eif Aquitaine	F	Bayer	D
Shell	NL	Asahi	J	AkzoNobel	NL
Allied	US	Akzo Nobel	NL	Mitsubishi	J
Cyanamid	US	Solvay	B	Air Liquide	F
Mitsui	J	Huls	D	Evonik	D
Ugine Kuhlmann	F	Mitsubishi	J	Sumitomo	J
Esso (Exxon)	US	Union Carbide	US	Mitsui	J
Celanese	US	DSM	NL	LG Chem	SK
Henkel	D	BP	UK	Toray	J

^a For country code, see bottom of Table 2.2.

TABLE 2.2 Fifty Top Chemical Companies in the World (2009)

Rank	Company	Headquarters Country	Chemical Sales (\$ million)	Chemical Operating Profit as % Chemical Sales	Chemical Sales as % Total Sales
1	BASF	D	54,817	3.5	77.6
2	Dow Chemical	US	44,875	3.9	100
3	Sinopec	RC	31,302	6.4	15.9
4	INEOS Group	CH	28,600	NA	100
5	ExxonMobil	US	26,847	8.6	8.9
6	DuPont	US	25,960	9.5	99.4
7	Formosa Plastics Group	TwN	25,437	6.5	61.9
8	Royal Dutch/Shell	NL/UK	24,586	NA	8.8
9	Sabir	SA	23,096	25.6	84.0
10	Total	F	20,521	3.8	11.2
11	LyondellBasell	NL	19,993	3.1	64.9
12	Bayer	D	19,551	3.8	45.0
13	AkzoNobel	NL	19,360	5.9	100
14	Mitsubishi Chemical	J	16,742	def	62.4
15	Air Liquide	F	15,303	NA	91.7
16	Evonik	D	14,030	15.9	77
17	Sumitomo Chemical	J	13,121	1.8	75.8
18	Mitsui Chemicals	J	12,892	def	100
19	LG Chem	SK	12,625	13.9	100
20	Toray Industries	J	12,450	2.8	85.8
21	Linde	D	12,447	26.6	79.7
22	Reliance	IND	12,240	14.6	27.9
23	PPG Industries	US	11,390	10.8	93.1
24	DSM	NL	10,962	13.7	100
25	Mosaic	US	10,298	23.7	100
26	Shin-Etsu Chemical	J	9782	12.8	100
27	Yara	Nwy	9763	12.1	100
28	Asahi Kasei	J	9452	3.5	61.8
29	Praxair	US	8956	30.8	100
30	Sasol	SAf	8954	def	54.6
31	Syngenta	CH	8420	22.9	76.6
32	Chevron-Phillips	US	8406	8.4	100
33	DIC	J	8090	3.7	100
34	Solvay	B	7935	5.9	67.1
35	Air Products	US	7766	15	94.1
36	Huntsman Corporation	US	7763	0.8	100
37	Braskem	Br	7633	9.2	100
38	Lanxess	D	7047	4.6	100
39	Tosoh	J	6711	2.1	100

(continued)

TABLE 2.2 (*Continued*)

Rank	Company	Headquarters Country	Chemical Sales (\$ million)	Chemical Operating Profit as % Chemical Sales	Chemical Sales as % Total Sales
40	Borealis	Aus	6569		100
41	Arkema	F	6193		100
42	Clariant	CH	6090	3.7	100
43	Rhodia	F	5617	5.4	100
44	ENI	I	5525	def	4.8
45	Showa Denko	J	5489	0.4	75.8
46	Merck KGaA	D	5348	18.1	52.0
47	Dow Corning	US	5093	NA	100
48	Celanese	US	5082	9.0	100
49	Eastman Chemical	US	5047	10.2	100
50	Hitachi Chemical	J	4860	8.4	100

Note: Aus = Austria, B = Belgium, Br = Brazil, CH = Switzerland, RC = China, D = Germany, F = France, IND = India, I = Italy, J = Japan NL = Netherlands, Nwy = Norway SA = Saudi Arabia, Saf = South Africa, SK = South Korea, Twn = Taiwan, UK = United Kingdom, US = United States.

Source: *Chem. Eng. News*, 3 August 2009, p.14.

Although the chemical industry is proliferating around the world, the largest companies are still concentrated in the United States, Western Europe, and Japan. In Table 2.2, seventeen countries are represented, notably Austria (1 company), Belgium (1), Brazil (1), Switzerland (3), Germany (6), France (4), India (1), Italy (1), Japan (10), Netherlands (3), Norway (1), China (1), Saudi Arabia (1), South Africa (1), South Korea (1), Taiwan (1), United States (12), and joint UK/Netherlands (1). In the first edition of this book, we said that future lists may well include companies from the Middle East and Southeast Asia, and Saudi Arabia, China, South Korea, and Taiwan indeed occur. Other relative newcomers include Huntsman, INEOS (acquired interests of Inspec who got them from ICI), Sinopec, Syngenta (agrochemical interests of Astra-Zeneca and Novartis), and Nova Chemicals.

Of the 20 top companies in 1990, only 8 remained by 2009 (shown in bold in the 1990 column of Table 2.1). The 12 “new kids on the block” are shown in bold in the 2009 column. Eight of the top 20 companies in 1970 (shown in bold in the 1970 column) also remained in 2009.

For many years the list was fairly stable. Three of the largest chemical companies in the world were the three arms of the pre-World War II German company, I.G. Farbenindustrie. This giant company was divided into BASF, Bayer, and Hoechst, after World War II. In 1995 Hoechst, troubled by the difficulties of the heavy chemicals industry in Europe in the 1990s, demerged its entire company into twelve independent companies. The flagship was supposed to be the pharmaceutical sector, which merged with the pharmaceutical sector of Rhone Poulenc, which

similarly demerged its petrochemical operation. The new company was called Aventis. In 1993, ICI demerged its pharmaceuticals, agrochemicals, and specialty businesses to form a new company, Zeneca. Zeneca then merged with the Scandinavian firm Astra to give AstraZeneca, but it has since sold its agrochemical interests to BASF. In general, the profitability of companies selling specialties is higher than that of those making commodity chemicals and the profitability of U.S. companies is higher than that of other companies. Table 1.9 broadly illustrates these trends.

Dow and DuPont occupy second and sixth places, respectively, in Table 1.9. Since the Dow–Union Carbide merger in 2001, the joint company has had higher sales than DuPont. Dow (the historic Union Carbide name has been dropped) is an efficient company with highly integrated processes and high annual chemical sales per chemical employee (\$480,000), a figure exceeded among the large companies only by BP (\$500,000), Lyondell (\$980,000), and Union Carbide (\$510,000) (1999 data). DuPont is known for supporting its marketing operations with strong technical service. In the 14th position in Table 2.2 is the largest Japanese chemical company, Mitsubishi Kagaku, formed from a merger between Mitsubishi Kasei, which occupied 14th position in 1991, and Mitsubishi Petrochemical. Sumitomo, Mitsui, and Toray merged shortly after. Japanese companies are relatively small and their profitability is the lowest in the industry. State-owned companies like the Italian ENI (position 44, at one time known as Montecatini Edison, then Montedison, then Enichem) are among the least profitable, in part because inefficient operations are often maintained simply to provide employment.

Chemical arms of petroleum companies include Total, Royal Dutch/Shell, ExxonMobil, and Chevron-Phillips. Thus ExxonMobil is the fifth largest chemical company in the world, even though its chemical sales are only 8.9% of the total for the company. ExxonMobil (formerly Esso) and Shell both are principally petroleum exploration, extraction, and refining businesses, but they increased their petrochemical interests over a 37 year period. Total was active on a smaller scale. BP showed a brief interest in following a similar path, but lost interest after 2000 and divested itself of most of its downstream chemical holdings.

Historic names such as Union Carbide and American Cyanamid have disappeared from the list. Union Carbide, which had originally taken its name from the calcium carbide it made to generate acetylene for acetylene-based chemistry, merged with Dow in 2001. American Cyanamid, which had originated with a pre-Haber process method for fixing nitrogen via calcium cyanamid, divested itself of various businesses, notably the sale of catalysts in 1988, pharmaceuticals in 1994, and agricultural products (to BASF) in 2000. The company survives but does not feature in the top 50 chemical companies.

In 1970, 19 out of the top 20 companies were either American or West European and this had risen to 20 out of 20 by 1976 (Fig. 2.7). By 1993, three Japanese companies had appeared among the elite. By 2000, this had risen to four. By 2009, this “natural order” had been overthrown. The top 20 included companies from Taiwan, Saudi Arabia, China, and South Korea. The top 50 also included companies from India, South Africa, and Brazil. Seven of the top 50 are neither American nor West European. In 1976, as noted, all the companies were American, West European, or

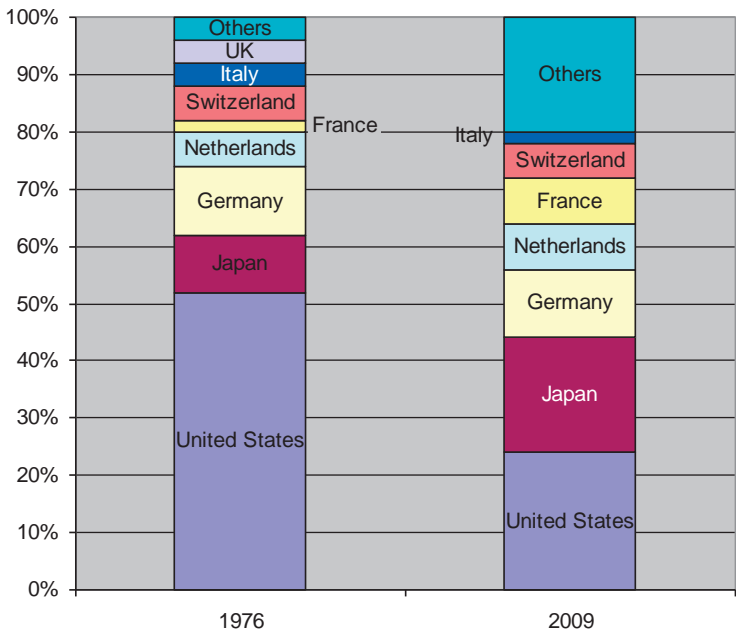


FIGURE 2.7 Top 50 chemical companies by nationality.

Japanese. In 1976, the United States housed over half of the major companies; by 2009, its share had dropped to under a quarter.

2.2.1 SulCIde of a UK Company

A restructuring of great impact was the trade in 1992 in which DuPont took on ICI’s European nylon business and ICI received in turn DuPont’s methyl methacrylate business and a cash payment. ICI then decided to reinvent itself as a specialty chemicals company and spun off its pharmaceutical and agrochemical divisions as Zeneca in 1993. In 1997, in an attempt to move into specialty chemicals, it purchased National Starch and Chemical, with an ageing portfolio, from Unilever, whence they also recruited a new CEO. It sold its heavy chemical assets, mainly to Huntsman, and resold the methacrylate business to a private equity company, INEOS, which is developing it aggressively. INEOS also bought ICI’s chloralkali business directly and had grown to a \$5 billion company by 2001. That left ICI primarily as purveyors of paint. Their corporate suicide was completed in August 2007, when AkzoNobel bought what was left of the company.

ICI was an international company, well placed to capture what profits were available from a commodity operation. It had an “ideal site” at Wilton/Billingham, with a refinery on site plus ethylene pipelines linking it to Grangemouth, Moss Moran, and Tranmere. It was surrounded by user industries, and its feedstocks and products needed only to be pumped over the wall. Britain is still a profitable market for home producers because of the costs of shipping. In 1986 ICI ranked fifth by turnover in the

UK industrial league table, with a return on capital of 21.9%; in 2000 it was ranked 108th in the UK with a return on capital of 20.1%. One is bound to ask if the transition, rather than a triumph for shareholder value (which was never achieved), was a failure of commercial nerve. Whatever the case, the shrinking of ICI and demerging of Hoechst and Bayer have significantly altered the structure of the European chemical industry (see Section 1.4).

2.2.2 Private Equity

Recent restructuring has been brought about in many cases by private equity firms. This is reflected in the table by INEOS and LyondellBasell. Such firms raise their funds from investors such as pension funds and insurance companies. The “private” in private equity means money that comes from these individual funds or wealthy individuals rather than money raised on the stock exchange. A private equity firm invests a portion of these funds and borrows the rest from banks. The advantage of private equity is said to be that it operates on a different timeline. Without having to meet quarterly financial reporting requirements — and expectations — private equity executives can take a longer term view of a company’s strategy, perhaps with a three to five-year time frame. It is thus less subject to the cyclical nature of the chemical industry.

The ethic of private equity firms is to turn around the company in those three to five years. Because a large proportion of the capital is not equity linked, the leverage is high and the subscribers to private equity stand to make worthwhile multiples of their initial investment. If interest rates are low, this is an attractive option, but the reverse also applies in a downturn, and it is easy to lose money. Most of the private equity companies have had difficulty meeting interest payments during the 2008/2009 recession. The consultants Ernst and Young point out that many private equity entrants into chemicals turned out to be unable to sell their companies when they wish to do so.² The value and volume of mergers and acquisitions in the first half of 2010 were the lowest for 15 years. One might still expect stock exchange listed companies to buy out private equity companies at a time when debt repayments become onerous, and BASF’s buyout of Cognis (a manufacturer of ingredients for cosmetics, toiletries, and foods) for 3.1 billion euros illustrates this point. As part of moving out of commodity plastics and into specialties, BASF also bravely bought Ciba in late 2008, the day that Lehman Brothers collapsed, starting the banking crisis of 2009.

Huntsman Chemical Corporation and INEOS are two of the more interesting private equity companies and their emergence illustrates the complexity of restructuring arrangements. The Huntsman Chemical Corporation was founded by Jon M. Huntsman in Salt Lake City in 1982 and is now run by his son Peter. The family are notable philanthropists.³ In 1997 Huntsman took advantage of the downturn to buy Texaco’s chemical interests for \$1.06 billion and then acquired Monsanto’s maleic anhydride and linear alkylbenzenesulfonate businesses and polypropylene from Eastman and Novacor. It bought ICI’s titanium dioxide and isocyanates businesses and sold polystyrene to Nova. By 2002 it found debt servicing difficult and went public in 2005. At the height of the private equity boom in

January 2007, it sold its UK plants to SABIC, and in July, it turned down an offer from Russian billionaire Leo Blavatnik, in favor of a better offer from Apollo (Hexion). Huntsman agreed to sell but Hexion then backed out on the grounds that Huntsman's finances were deteriorating. By February 2009, Huntsman's shares had lost 90% of their value, underlining the point about highly geared private equity. Meanwhile, in an attempt to restore value, Huntsman's Textile Effects Division acquired the Baroda Division of Metrochem Industries, as part of a realignment of Huntsman's manufacturing footprint toward Asia.

INEOS is a remarkably new firm to be ranked number 3 in the world list. It was formed in 1998 by entrepreneur Jim Ratcliffe to effect a management buyout of the former BP petrochemicals assets in Antwerp, Belgium, and it has since purchased several other BP divisions together with much of the dying ICI. It tries to take over businesses that other chemical companies think are not part of their core portfolios and has also acquired bits of Amoco, BASF, Dow Chemical, Solvay, and UCB. In October 2005 it agreed to purchase Innovene, BP's olefins and derivatives and refining subsidiary, which had an estimated 2005 turnover of \$25 billion, for \$9 billion. The deal roughly quadrupled INEOS's turnover, which was previously around \$8 billion, and took BP largely out of the chemicals business. By 2008 sales had reached about £23 billion but slumped to £16 billion in 2009 as a result of the recession. INEOS faced major problems in refinancing its £6.4 billion debt (€7 billion). After several nerve-racking months, by what appeared the commercial equivalent of walking on water, it refinanced part of its debt by a €1 billion bond issue, and changed its official domicile from the United Kingdom to Switzerland, saving an estimated £450 million in tax between 2010 and 2014. Royal Dutch/Shell is registered in the Netherlands, so that, for the first time in the history of the chemical industry, the United Kingdom is without a representative in the top companies.

Another aspect of restructuring is realignment of business segments. As an example, Union Carbide had a small, and presumably barely profitable, polyether polyol business. Carbide sold this business in the early 1980s to ARCO, a major manufacturer of the propylene oxide from which the polyols are made. ARCO not only gained more captive use for its propylene oxide but increased its polyether polyol business well above the critical mass. In spite of this, in 1999 ARCO was bought by Lyondell. Both of these companies had been spun-off by Atlantic Richfield, which later was acquired by BP, itself a union of British Petroleum and Amoco. Lyondell, like other petroleum companies, does not look kindly on products that are far downstream from the refinery and sold the polyether polyols business to Bayer. Bayer, one of Germany's big three chemical companies, announced in 2001 its aim "to become known as a pharmaceutical company with a chemical business rather than a chemical company with a pharmaceutical business," but its cholesterol-lowering drug Ciprobay had to be withdrawn from the market after being implicated in a number of deaths. Even though ciprofloxacin had huge success as an anti-anthrax drug during the scare about unconventional weapons and terrorism, Bayer has felt compelled to demerge into four operating subsidiaries and to sell other operations. Hoechst, another of Germany's big three, demerged itself into twelve separate companies, as noted above.

Yet another restructuring is the combination that started in 1983 when Montedison and Hercules merged their polypropylene businesses to form a new company, Himont. After four years Montedison bought out Hercules's share. In 1994 the Montedison and Shell polyolefins businesses combined to form Montell, which became the world's largest polypropylene producer. Shell then took back the polyethylene business and formed a joint venture with BASF called Elenac. Montedison then sold its remaining share of Montell back to Shell, which became the sole owner. To meet the enhanced polypropylene competition, Hoechst and BASF in turn merged their polyolefins businesses and called the joint venture Targor.

Subsequently, Targor and Montell merged to become Basell Olefins. Meanwhile Equistar, which had been formed as a three-way venture between Millennium Chemicals, Occidental Chemicals, and Lyondell in 1997/1998, and which had extensive polyethylene interests, passed entirely into the hands of Lyondell.

Basell was highly polypropylene oriented, and Basell in Western Europe was 2.4 times as large as the next largest producer, Borealis. Borealis was itself a joint venture of the Finnish company Neste and the Swedish company Statoil. Neste subsequently left the business by selling its portion to the state-owned petroleum company of Abu Dhabi and the Austrian company OMV. Subsequently, Amoco and Appryl merged their polypropylene businesses in Europe to become somewhat larger than Borealis.

In 2005, Leo Blavatnik, founder and chairman of Access Industries, frustrated in his attempt to buy Huntsman, bought Basell instead. In 2007, Basell bought Lyondell to become LyondellBasell Industries (LBI). And the happy ending? In January 2009, LBI's U.S. operations had to file for Chapter 11 bankruptcy protection and emerged from bankruptcy in April 2010.

The Byzantine complexity of these maneuvers typifies the restructuring that has gone on in the chemical industry over the past 20 years. The sad thing is that little if any of this activity has enhanced stockholder value or increased profitability. The only thing it might do is enhance creativity, but creativity is inhibited and researchers demoralized by repeated takeovers, mergers, buy-backs, and the other activities, with the associated cultural change that financial experts regard as the solution to the industry's problems. The percentage of sales devoted to research and development, averaged over 17 companies, dropped from 5.7 in 1993 to 3.9 in 2002 to 2.9 (estimated) in 2006. Few companies own a facility long enough to undertake the long-term research that innovation requires, although that does not apply to long-term survivors such as Dow, Dupont, and BASF.

2.3 PARTICIPATION IN INTERNATIONAL TRADE

The chemical industry in the United States always had two advantages, which made its products cheap not only at home but also in the international arena. First, there was ample natural gas, which provided ethane and propane for steam cracking (Section 4.5.1), and it generally was cheaper to crack gas than the liquids, naphtha and gas oil. Second, the United States had ample supplies of propylene, not only because it is produced in steam cracking, but because the huge capacity for catalytic cracking

(more than the rest of the world combined) required by the gasoline industry means that the few percent of propylene produced in this reaction translates itself into millions of metric tons of product (Section 4.6).

In spite of this, on the face of it, the European Union has a far healthier trade balance than the United States: in 2009, world trade in chemicals amounted to €1871 billion, of which the European Union claimed 24% or €449 billion. In 2009 world chemicals sales amounted to €1871 billion, of which the European Union 27⁴ contributed 24% or €450 billion of which €117 billion was exports outside the EU. Approximately €222 billion was intra-EU trade and only €110 billion was domestic trade. Western Europe exported 73% of its production if one counts intra-European trade and 26% if one excludes it. Companies like BASF, LyondellBasell, Degussa, Akzo Nobel, and Evonik are all highly export-oriented. High levels of exports are required if plants are to operate efficiently, even if exports are rarely as profitable as home business.

In 2009 the United States exported \$154.6 billion against \$155.4 billion imports, giving a negligible trade balance. The value of exports and imports has nonetheless risen over the previous decade from about \$70 billion, that is, it has almost doubled in real terms. This increase is reflected worldwide and indicates the extent of globalization.

It should be noted that the economic figures given here and elsewhere in this book should be treated with modest skepticism, especially when different countries are being compared. The figures are affected by who gathers them, by exchange rates that vary during a year, by differing accounting conventions, and so on. The euro:dollar exchange rate varied between 1.59 and 1.26 over the period January 2008 to January 2010. Sets of data over a number of years and compiled by the same people may illustrate trends but, for example, the expansion of the European Union from the six founding states to the present 27 has distorted the statistics, even though the new eastern European countries have only small chemical industries. The American figures here are taken from the United States Statistical Abstract and the European ones from CEFIC, but Chemical and Engineering News and the Guide to the Business of Chemistry also produce figures that differ from each other. Chemical industry statistics may include or exclude pharmaceuticals and polymers—the above European figures exclude pharmaceuticals but not polymers and are about a quarter basic organics. The problem becomes more acute when authoritarian regimes are concerned. Veterans of the Cold War will remember the distortion of USSR statistics to indicate that economic planning was working, and it is unclear how reliable are the published statistics for China.

The implication above that the European Union chemical industry is thriving at the expense of the U.S. industry, however, is misleading, certainly insofar as the petrochemical industry is concerned. Specialties and consumer chemicals are responsible for 40% of the trade balance. All basic chemicals make up only 25%. Furthermore, many U.S. companies, especially pharmaceutical companies, operate subsidiaries in the European Union to avoid tariffs. Some of them export to the United States and depress its trade balance. The U.S. chemical industry's international

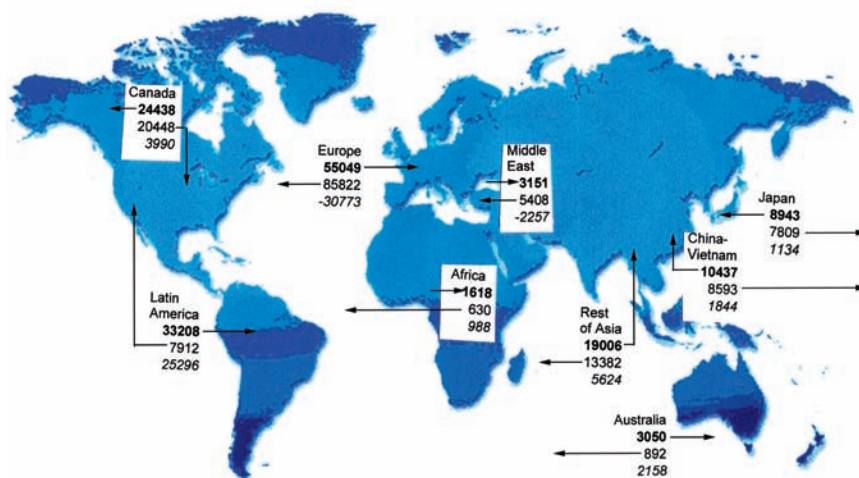


FIGURE 2.8 United States 2009, exports (in bold), imports (in roman), and balance of trade (in italics). (Source: Nexant Inc.)

investments provide appreciable income from the net earnings of foreign subsidiaries and from the licensing of U.S. technology to those subsidiaries as well as to other companies.

In spite of the increase in its favorable trade balance from €39.2 billion to €42.6 billion, the recession of 2009 hit the European industry hard, with sales down by almost 20%. It is dependent on liquid feedstocks and its steam crackers are not flexible. Its position is deteriorating with key countries in Asia. As noted in Figure 2.2 Asia-Pacific has risen from a region with a substantial negative trade balance ten years ago to a positive balance today.

Nor should the United States' poor trade balance be allowed to denigrate the role of U.S. exporters. In 2009, the chemical industry was the second largest U.S. exporter after the machinery sector. Ten percent of exports were chemicals and amounted to \$159.7 billion. The United States' balance of trade dropped over the early 1990s because the strength of the dollar meant that imports were cheap, exports expensive, and there was increasing competition from less developed countries, but there has not been an adverse balance of trade since 2006. The United States' imports, exports, and balance of trade with various geographic regions are shown in Figure 2.8 and similar data for Europe are shown in Figure 2.9.

Japan, having based its chemical industry on relatively expensive imported naphtha and having struggled with an expensive yen, cannot compete in the world market, although since the mid-1990s it has enjoyed sales to neighboring countries with expanding economies, primarily China. Freight costs are a significant additional expense in the heavy chemicals business and Japan's geographical position enables her to compete in the Far East, but this has contributed little to profitability.



FIGURE 2.9 Extra-EU chemicals trade flows with major geographic regions (billion euros, 2009). (Source: CEFIC.)

2.4 COMPETITION FROM DEVELOPING COUNTRIES

But what about the future? Many countries have petroleum, and huge deposits of natural gas have been discovered relatively recently in many places in the world; Russia and Qatar now have the largest reserves. Some, if not most, of these countries, are eager to enter the chemical business because it promises greater value added than is possible when the gas or oil is used for energy. Thus an awesome list of countries has built or is building chemical industries. The United States, Western Europe, and Japan have long standing industries. Newcomers in the 1980s included Saudi Arabia and other Gulf states, Canada, Mexico, Venezuela, Brazil, Argentina, and other Latin American countries including Trinidad and Chile, the former members of the USSR and other Eastern European countries, and the “tiger” economies of Southeast Asia. Taiwan and Korea had to import feedstocks, but Thailand, Indonesia, and Malaysia had indigenous resources. China’s oil industry is mature and production has peaked. Singapore had no raw materials and no indigenous market, but an excellent infrastructure and stable and relatively honest government. How seriously some of these countries regard the chemical industry is indicated by the statistic that in Taiwan the chemical industry accounts for 30% of manufacturing as opposed to 10% in the United States and Western Europe. Many of these countries entered the chemical business to provide for their own needs. Taiwan and Thailand indicate that they will not be major exporters because they can consume locally most of their production. Korea, Saudi Arabia, Canada, and most other countries have become formidable competitors in the international trade arena. The impact on Western European trade of recent entrants to the petrochemical market, and particularly Canada and Saudi Arabia, is indicated in Figure 2.10, which shows an increasingly unfavorable trade balance in ethylene and benzene derivatives and a decreasing positive balance in

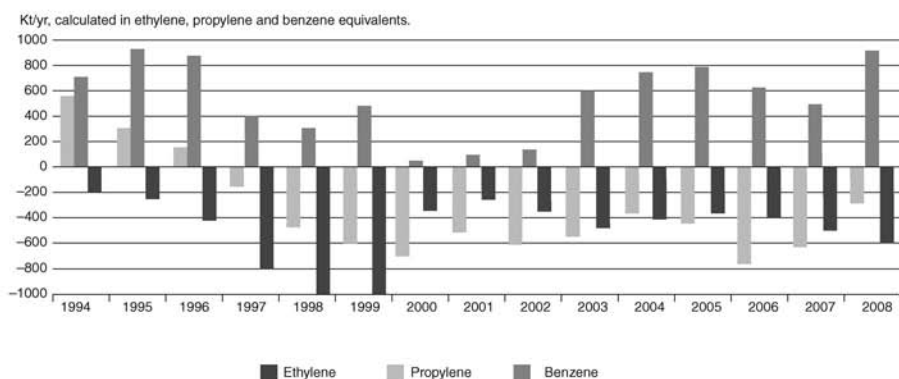


FIGURE 2.10 Western European trade balance of petrochemical derivatives (thousand metric tons per year in ethylene, propylene, and benzene equivalents). (Source: CEFIC, <http://www.petrochemistry.net/10.2.html>.)

TABLE 2.3 Decline in Production of Petrochemical Ethanol in the United States

	1982	1985	1988	1990	1999	2000	2001	2007
Thousand metric tons	464	260	227	95	95	82	82	56
Million gallons	2226	1247	1088	457	457	392	392	270

propylene derivatives. These figures are perhaps a better measure of the problems of the European petrochemical industry than the favorable overall trade balance.

The significant features of this figure are first the adverse trade balance of ethylene derivatives from about 1999 onwards, the positive balance in propylene derivatives, and the surprisingly poor trade balance in benzene derivatives, bearing in mind that the Europeans catalytically reform substantial amounts of benzene from naphtha. This last is related to the cracking of naphtha as opposed to natural gas liquids, and to the decision by the Saudis only to crack ethane.

The United States still maintains a role and it is believed that this might continue indefinitely, as noted above, if shale gas resources for steam cracking (Section 4.5.1) are as exploitable as claimed. The situation is unpredictable. Prices of both oil and gas fluctuate. They were exceptionally volatile in the 2000s; the present trend is that oil is becoming more and gas less expensive.

The impact a developing country can make is exemplified by the declining production of petrochemical ethanol in the United States. The data are shown in Table 2.3. Admittedly, the use of ethanol as a chemical feedstock is declining, and use of subsidized corn-based fermentation ethanol for fuel is increasing. Nonetheless, Saudi Arabia's cheap ethylene can be converted to ethanol and imported into the United States at a cost that makes its domestic manufacture uneconomic. Freight costs make it uneconomic to import practically any other Saudi basic chemical into the United States. The virtue of ethanol is that its molecule contains a high proportion of ethylene (59%) so that ethanol can be thought of as a cheap way of shipping ethylene. It was predicted that petrochemical ethanol manufacture in the United States would come to an end by the year 2000, but a single producer—Equistar—remained in the field, certainly until 2007 and probably until 2010, when the plant suffered a major fire. Equistar is a subsidiary of Lyondell Chemical, the U.S. arm of LyondellBasell, and was involved in messy bankruptcy proceedings (Section 2.2.2). Fermentation ethanol boomed as MTBE (Section 7.2.1) was phased out. At the time of writing, the U.S. government subsidizes fermentation ethanol as a gasoline additive to the extent of \$0.119/liter (\$0.45/gallon) and the subsidy primarily goes to the alcohol manufacturers, while the farmers get only about 13%. Use of subsidized fermentation ethanol for chemical production is illegal as is the use of petrochemical ethanol in drinks.

As already indicated, numerous other countries have entered the chemical business but Saudi Arabia is impressive for two reasons. First, it has over 20% of the world's oil reserves; and second, it has a reasonable supply of so-called associated gas (ethane, propane, and butanes), the gas that comes out of the ground when oil is pumped. Since

there is no alternative use for this gas in Saudi Arabia, it has zero value at the wellhead. The Saudis decided to extract and crack the ethane at an extraction cost of \$0.50–0.75/million BTU (British thermal unit; 1 BTU = 1.054 kJ) and to sell the LPG (propane + butane) on the world market. This provides extremely favorable economics for ethylene production. Iran is possibly less efficient and costs its ethylene at \$1.25/million BTU. In 2002, the Middle East produced about 28 million metric tons of ethylene, half from Saudi Arabia, a fifth from Iran, and 30% from all other producers, principally Kuwait and Qatar. SABIC alone was producing 8052 million metric tons by 2009, that being 7% of world production.

To become a full player in the world petrochemical market rather than just dealing in ethylene derivatives, the Saudis also built a plant to crack $C_3 +$ and condensate (a cheap $C_5 +$ fraction from certain gas wells) in 1995 and declared that a 30% discount off the lowest export price would be granted on supplies of naphtha, condensate, and LPG used in their newest petrochemical plant.

There is no moral reason why developing countries should not take trade away from developed countries when able to do so. Developed countries stay ahead by innovative technology and, once that technology has become mature and is free of patent coverage, anyone is entitled to use it. Many companies in the developing world, however, undercut costs by ignoring health and safety precautions. Frequently, the companies or contractors that build these plants are from the developed world, and they would claim that, by building them, they are providing employment for very poor people and helping the developing countries that are concerned. It is uncertain whether there are genuine cost savings by neglect of precautions or whether this is merely an excuse for poor performance by companies in the developed world. As the Middle Eastern and Southeast Asian chemical industries expand, this moral problem grows, but no solution is in sight.

ENDNOTES

1. ICIS News, 21 April 2011, <http://www.icis.com/Articles/2011/04/21/9454636/dow-chemical-to-build-new-us-cracker-for-start-up-in-2017.html>.
2. <http://www.altassets.com/pdfs/EYchechemicalsjune04.pdf>.
3. http://www.huntsman.com/eng/Aboutus/Brief_history/History_in_the_00's/index.cfm?pageID=7431.
4. In 2004, the European Union expanded from 15 to 27 countries, with the accession of eastern European states.

CHAPTER 3

Transporting Chemicals

Raw materials for chemicals will generally be derived in one location, refined at another, and the downstream products manufactured at possibly several locations. These products, for example, polymers, will then be processed further, probably in many different additional locations, before they end up as plastics goods, automobile tires, textiles, paints, and so on. Chemicals share with many other commodities the general problems of transportation¹ – they must be delivered on time and in perfect condition – but they present additional hazards because they are frequently highly flammable and/or toxic. Over the years there have been a small but significant number of high profile chemical transport accidents. Methods of transport must be safe for the delivery staff, the general public, and the environment. To ensure this, about 10% of the turnover of the petrochemical industry is spent on transport/logistics. The factors applying to petroleum and natural gas differ from those governing chemicals and will be considered separately.

3.1 SHIPPING PETROLEUM

Petroleum is one of the major commodities traded internationally (Fig. 3.1). Consumption occurs mainly in the industrialized West and Japan, while production takes place largely in the Middle East, the former Soviet Union, West Africa, and South America. Imports by China are increasing rapidly.

Petroleum is moved mainly by two methods: oil tanker ships and oil pipelines. More than three-fifths moves by sea and under two-fifths by pipeline. The development of large tankers (>300,000 metric tons DWT²) has made intercontinental transport of oil possible; tankers are low cost, efficient, and extremely flexible. Oil pipelines can only compete with sea transport if the pipeline route is considerably shorter than the sea route. The choice is made on economic or strategic grounds.

The cost per mile per metric ton of moving petroleum by tanker does not vary enormously with quantity transported. The cost per metric ton-mile decreases

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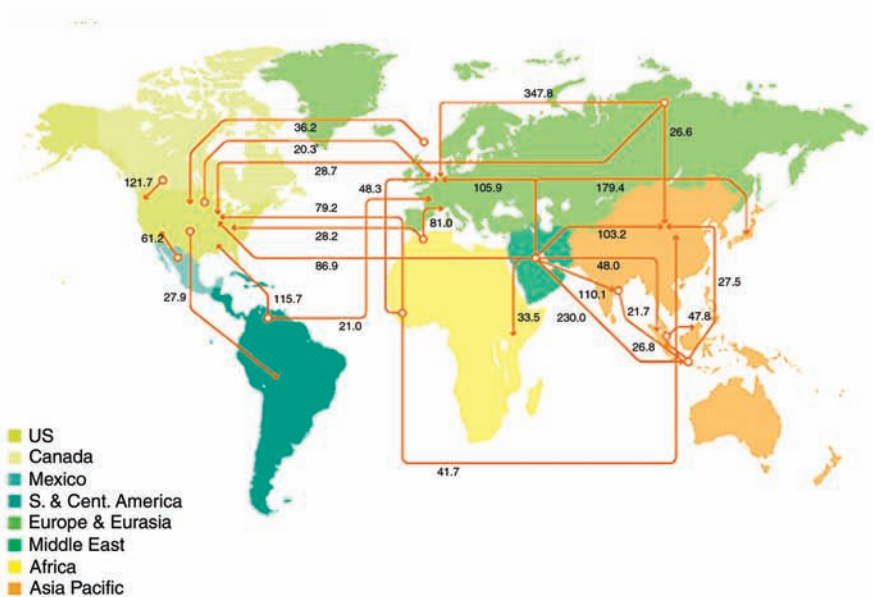


FIGURE 3.1 Worldwide flows of oil 2009 (millions of metric tons). (Source: BP Statistical Review of World Energy.)

somewhat with distance but, of course, the overall cost increases. Economies of scale are chiefly achieved by use of the largest practicable transport unit.

Pipelines have the opposite characteristics. Capital costs are high and operating costs relatively low. At a rough estimate, operating costs are divided more or less equally between labor, maintenance, and so on, and the remainder comprising power consumption. The transportation cost drops rapidly with pipeline capacity. This is partly because a doubling of pipeline diameter only doubles the amount of pipe required but quadruples the capacity, but also because the cost of laying and operation is relatively insensitive to scale.

Privately owned pipelines have the advantage that they are not subject to charges at their entry and discharge terminals. Public (i.e., owned by consortia) pipelines such as Sumed (oil) and ARG (Aethylen Rohrleitungs Gesellschaft mbH) charge customers, while marine tankers are subject to harbor dues, and road and rail tankers to depot loading charges.³

The disadvantage of pipelines is that once laid it is not possible to change their destination. They are only suitable where both supply of and demand for whatever is to be transported can be maintained long enough for the capital costs to be recovered.

Thus for transcontinental overland petroleum movements, pipelines remain the mode of choice and are at least an order of magnitude cheaper than options such as rail, barge, or road. They are also needed to bring the oil from wellhead to gathering point – to an ocean terminal or a refinery. They are critical for landlocked crudes and complement tankers at certain key locations by relieving bottlenecks or providing shortcuts.

The choice between pipelines and tankers is also affected by strategic considerations. Pipelines are attractive if political constraints do not exist, but they are vulnerable to terrorist attacks in areas of political instability. For example, the late Osama bin Laden called on his cohorts to target “the oil resources that do not serve the nation of Islam.” In the two years after the so-called end of major hostilities in Iraq in April 2003, there were about 200 pipeline attacks, mainly in northern Iraq, primarily on the pipeline running from Kirkuk to the Turkish Mediterranean terminal of Ceyhan. Other attacks have occurred in Nigeria, Mexico, and Balochistan. In British Columbia, the pipelines of the gas company EnCana were bombed six times in 2009, and the company was given three months to cease operations or face new attacks. The Egypt–Israel pipeline was bombed in April 2011 in the disorganization following the “Arab Spring.”

The Suez Canal provides an interesting comparison between pipelines and tankers. It is 195 km long and 60 m wide and was closed from 1967 to 1975 because of the Arab–Israeli Six-Day War. Its use can be avoided. During its closure, some oil companies decided to take the long sea route around the Cape of Good Hope, using 300,000 metric ton DWT tankers, which were anyway unable to navigate the Canal, which was limited to tankers of up to 150,000 metric tons DWT. Also, a pipeline – the Sumed pipeline – was built parallel to the Canal. Oil flows in the early 2000s totaled about 180 million metric tons/year of which 125 million metric tons/year went through the pipeline and 65 million metric tons through the Canal. The Cape route adds greatly to the journey time for transport to Europe but is still extensively used

for oil exports to America and Australia.⁴ Shipowners have to calculate whether a long sea voyage is cheaper than a short one plus the Suez Canal charges. For example, Rotterdam to Melbourne is longer via the Cape but ultimately cheaper because it avoids Suez Canal charges on the order of \$120/metric ton.

Tankers, on the other hand, are subject to piracy, which is an attractive option (for pirates) around maritime “chokepoints” such as the Strait of Hormuz leading out of the Persian Gulf, and the Strait of Malacca between the Malaysian Peninsular and the Indonesian island of Sumatra. This links the Indian Ocean (and oil coming from the Middle East) with the Pacific Ocean (and major consuming markets in Asia). Other important maritime “chokepoints” include the Bab el-Mandab passage from the Arabian Sea to the Red Sea, and the Suez Canal, connecting Port Said on the Mediterranean with Suez on the Red Sea (Fig. 3.2).

Piracy in lawless Third World countries is an economic option, as opposed to pipeline attacks, which are political. Tankers and their cargoes are valuable and vulnerable; their crews are few and ill-equipped for warfare. Oil companies are willing to pay huge ransoms to recover their craft plus its contents. Increased patrols by Indonesia, Malaysia, and Singapore have reduced incidents in the Strait of Malacca,⁵ but the collapse of the fishing industry off the horn of Africa has led to a huge increase in Somalia-based piracy.⁶ Overfishing has depleted fish stocks off the coast of Somalia, and 1500 Somali fisherman are estimated to have turned to piracy. In the first six months of 2011, there were 266 attacks compared with 196 in the same period in 2010. Sixty percent of the attacks were carried out by Somalis. In the two years to April 2011, 150 vessels had been hijacked and 500 hostages taken and held for an average of 150 days. Ransoms paid have amounted to \$160 million/year, but the cost to the global economy is estimated at \$7.6 billion/year. This may be an exaggeration, but rates per ship appear recently to have risen to an average of \$4 million,⁷ with a record of \$9 million.

3.2 SHIPPING GAS

For many years, the development of reserves of natural gas and gas liquids was inhibited by the high cost of transportation. Natural gas has about 1/900 of the thermal



FIGURE 3.2 Location of piracy incidents, first half 2009. (Source: *London Times*.)

density of crude oil, and a given pipeline can carry only one-fifth the amount of gas, measured by its heat content, as it can oil. Better welding techniques, larger pipe diameters, and higher operating pressures have since extended the range over which gas can economically be transported, and these methods are used in the United States and Europe for intracontinental transport.⁸ Worldwide flows are shown in Figure 3.3. The main importers are the same as for oil, but exporters include Australia, Canada, and Scandinavia, among others. The largest reserves are in Russia and Qatar.

Even then, many reserves are uneconomically distant from the market (“stranded gas”) and, apart from the possibility of gas-to-liquid processes (Section 12.7), such gas can also be transported by liquefaction. For natural gas, the practice is to liquefy at -162°C and atmospheric pressure. The first refrigerated tanker to be built was the *Methane Princess* in 1964, which shipped LNG from Algeria to the United Kingdom, where it was stored in a cavern under the Isle of Grain in the Thames estuary and confined by the permafrost that formed around the cavern. The modern terminal involves above-ground full containment LNG storage tanks with a capacity of almost 10 million metric tons/year. Refrigerated tankers cost on the order of \$1 billion – about three times as much to build and operate as normal tankers – and freight charges for gas are correspondingly 2–3 times as high as for liquids.⁹ Typically, between 0.1% and 0.25% of the LNG boils off each day. The gas produced was traditionally diverted to the engines and used as a fuel for the vessel. Modern tankers have reliquefaction plants, and the tankers are powered by slow speed diesel engines, which are more efficient and environmentally friendly than the traditional steam turbines. The LNG must be regasified at its destination.

3.3 SHIPPING CHEMICALS

More than half of the tonnage of chemicals in the United States is transported less than 250 miles. This applies especially to bulk low-value added commodities, such as fertilizers and bulk inorganics, and also to gases, which are typically pumped “over the fence” and are not even included in transportation statistics. Pharmaceuticals, consumer products, and specialties are liable to be transported longer distances.

Chemicals may be transported overland by pipeline, rail, road tanker, or river barge. The proportions of chemicals shipped by the various methods are shown by tonnage and by cost in Figure 3.4.

3.3.1 Gases

In the United States, there is a huge network of pipelines carrying ethylene, propylene, and C_4 hydrocarbons. Figure 3.5 shows the Texas pipeline system. Ethylene is transported as a gas at pressures on the order of 100 bar. Pipes are typically 300 mm in diameter. Europe has a related but smaller ethylene network shown in Figure 3.6. These are “common” networks, shared by the major producers. ARG is the major operator and its 495 km pipeline transports ethylene between producers and consumers at petrochemical sites in Germany, Belgium, and the Netherlands. It links

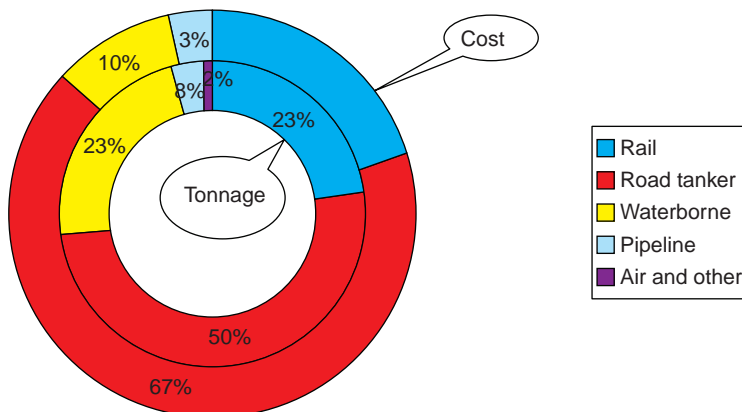


FIGURE 3.4 Transportation of chemicals by mode (internal United States 2008). Tonnage: 764 million metric tons; value: \$37.9 billion. “Other” includes pipeline, air, and intermodal transportation. More than three-quarters of the category is pipeline transportation of ethylene and oxygen, usually for short distances. (Source: Guide to the Business of Chemistry, 2009.)

directly or indirectly almost half the ethylene production capacity in Europe and 90% of the capacity in Belgium, Germany, and the Netherlands. Plans to pipe propylene appear to have been shelved.

Detailed maps of the various pipeline systems worldwide are available.¹⁰ Although this is not apparent from the “spaghetti bowls” of pipelines illustrated in these maps, the majority of gases are “pumped over the fence” and used close to the point of production. Transporting gases over appreciable distances may be too hazardous and/or too expensive. Gas ocean freight costs two to three times liquid freight, and pipeline charges are pitched at a level to keep them competitive with batch transfers. For example, to ship 3000 metric tons of ethylene from the Tees (Middlesbrough) to Saltend (Hull) in the United Kingdom, a distance of about 120 miles, would cost of the order of \$30–40/metric ton. Pipeline costs would be somewhat less. The same quantity of benzene would cost \$15–20/metric ton, and to send 1 metric ton of ethylene 30 miles on the European grid would cost about 30 euros (\$42). Compressed gases in pressurized cylinders can be shifted by the normal methods for freight.

3.3.2 Liquids

Liquids can be shipped inland by pipeline, rail, road tanker, or river barge. Deliveries by sea are performed by so-called parcel tankers. Road tankers have been gaining market share in recent years because they offer flexibility and quick delivery. They are also used for the more expensive unit value products.

Very few pipelines over 20 km long exist for liquid chemicals, although they are frequently used for transfer between neighboring plants. Meanwhile, the trade in methanol (Fig. 3.7) is carried out almost entirely by marine tanker. The reason is that

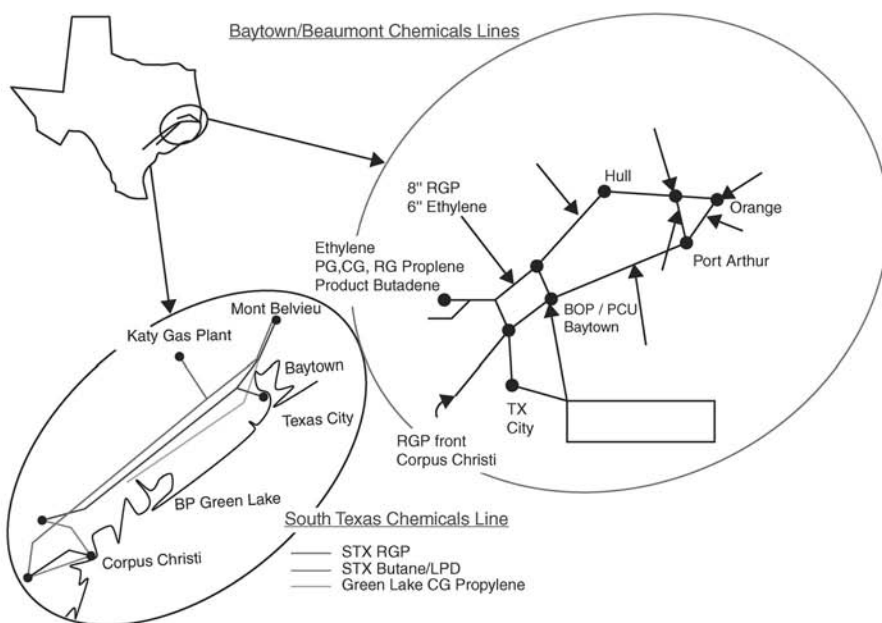


FIGURE 3.5 The Texas pipeline system. (Source: Nexant Inc.)

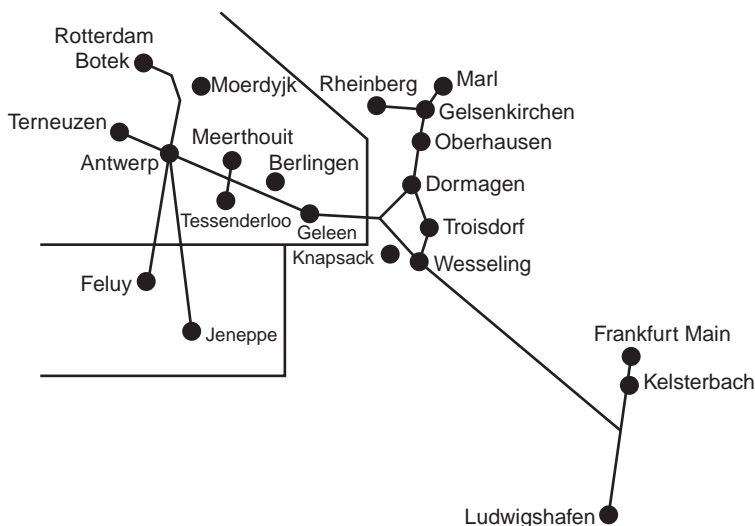


FIGURE 3.6 Common ethylene pipeline grid in Western Europe. (Source: Nexant Inc.)

conversion to methanol is a way of using “stranded” natural gas, which, by definition, originates a long way from where it is needed.

Chemicals can be shipped by river barge where a suitable waterway is accessible. Figure 3.8 shows a container barge on the Seine, but in general in Western Europe, barge transport means the rivers Rhine and Schelde linking, for example, Rotterdam, Antwerp, and Ludwigshafen. Exxon and other Rotterdam/Antwerp producers ship aromatics to the Rhine-based consumers in the Duisberg/Ludwigshafen area, and the barges then return with derivatives such as acrylates and solvents for distribution and/or pumping into vessels for export. The river will take cargoes from 1000 to 3000 metric tons DWT. A light barge will sit too high in the water and might foul a bridge over the river. Too heavy a barge might run aground. High and low levels of river water present similar hazards. Barges are made in standard sizes so that they can be “rafted” together.

The Danube is the other major waterway in Europe and carries much traffic, although the chemical side awaits the further development of chemical industries in Eastern Europe. Meanwhile, at a time when canal building has an eighteenth century image, it was thought worthwhile to build the Danube–Black Sea Canal in 1984 and the Main Canal in 1992 (“Main” pronounced as in “coal *mine*” not “*main* line”). This links the Rhine and the Danube for the first time and provides a water link between the North Sea and the Black Sea. So far, the major chemicals shipment has been fertilizers but this is expected to change. Regrettably, the Danube was seriously polluted by the bombing of Serbian chemical plants during the Kosovo conflict.

The United States has huge waterways that can be used for waterborne traffic, including the Mississippi, Tennessee, Ohio, and Missouri waterway systems. Towed barges on these waterways account for the majority of traffic, with coastal and lake ships accounting for the remainder.

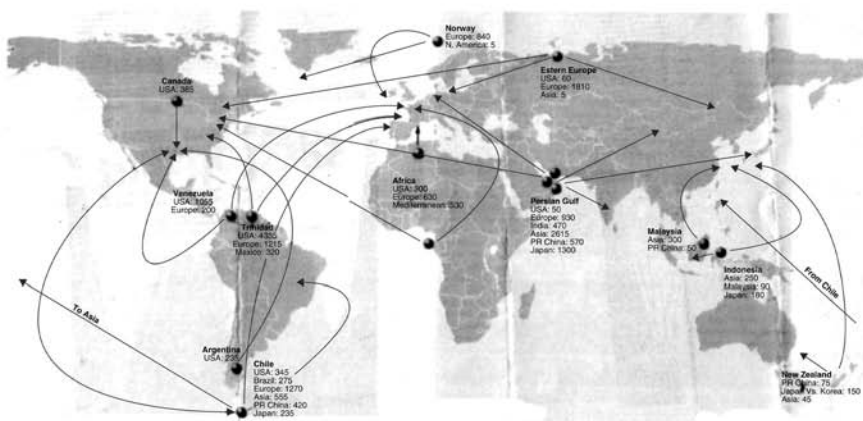


FIGURE 3.7 World methanol trade 2006 (thousands of metric tons). (Source: Methanol and Derivatives Global Outlook 2000–2012, PCI Ockerbloom & Co. Inc., *Chem. Week*, 7/14 July 2008, p. 46.)



FIGURE 3.8 Container barge on the Seine.

Details of U.S. waterborne commerce are given by the Waterways Council Inc.¹¹ In 2006, 627 million metric tons of goods were shipped on inland waterways, 25% being petroleum and petroleum products and 8% chemicals. As may be deduced from Figure 3.4, the average value of cargoes is \$50 per metric ton. Waterborne transport is cheap and used largely for low cost materials.

Inland sites away from river or railway can be serviced straightforwardly by road tankers, typically carrying between 18 and 20 metric tons depending on the density of the liquid. Some tankers are fitted with heating coils so that, for example, phthalic anhydride (melting point 130.8°C) can be transported and pumped as a liquid. This is important because, when used in plasticizer synthesis, the phthalic anhydride must have as good color as possible. Solidification followed by remelting would cause yellowing. Some tankers are partitioned so that several liquids can be carried. Some tanks can be loaded and unloaded to permit door-to-door deliveries and exchange of loads with other forms of transport.

Rail tank cars may also be acceptable if loading/unloading facilities are available. They vary in size from 18 to 95 m³ and may be made of stainless steel, aluminum, or mild steel with an inner rubber, thermoset plastic, or enameled liner. They may also be uncoated. There are also crash protected rail cars for chlorine fitted with protective shields to serve as crumple zones and to protect the tank bottoms from perforation. Some cars are fitted with automatic brakes that come into operation if the tank car is derailed.

For inland transport of liquids, the modern trend is toward flexibility and compatibility. Tanks are designed so they can be unloaded as self-contained units and can be transferred to another form of transport—truck, ship, and so on—without disturbing the contents. This is helpful for door-to-door delivery. Tanks for this purpose have to comply with International Standards Organization regulations and are called ISO tanks (Fig. 3.9). They hold water, foodstuffs, hydrogen peroxide, gases, and other materials, both hazardous and nonhazardous. For more volatile substances, refrigerated ISO containers with specialized linings are available. For compounds that need to be kept liquid, there are heated ISO containers. These tanks are generally 6.1 m (20 ft) long and are the same size as general purpose containers. They may be carried on rail cars (Fig. 3.10) or on trucks (Fig. 3.11) or take their place on container ships or barges.

Drums and packages may be used for smaller volumes where the receiver does not have bulk receiving facilities or where consumption is generally less than



FIGURE 3.9 ISO tank for transporting liquids. (Courtesy of Suttons Group.)

~500 metric tons per annum. Tanker operators and/or producers of chemicals have facilities for putting chemicals into drums of up to 1000 liters or plastic containers. The conventional drum is a 90 cm high by 60 cm diameter cylinder and contains 210 liters (55 U.S. gallons). Twenty-five liters is a convenient size for plastic



FIGURE 3.10 Loading ISO tanks onto rail cars. (Courtesy of Hoyer Group.)



FIGURE 3.11 ISO tank on truck. (Courtesy of Suttons Group.)

containers. At intermediate levels of consumption, drums loaded into containers compete with ISO tanks, and the Stott Nielsen website¹² goes to considerable trouble to demonstrate that ISO tanks are more economic.

Long distance sea transport of liquids is performed in large parcel tankers with DWT above 20,000 metric tons. These ships might contain 20–30 different chemicals. There must therefore be careful segregation of different grades of chemicals, and a ship will typically have 30–40 separate tanks, all of which have dedicated pumps and inlet and outlet lines so that losses in transit and by contamination are rare. Tanks may be made of stainless steel, which will carry anything but is expensive, or zinc silicate coated mild steel, which is cheaper but less versatile. Some tanks will be fitted with heating coils to keep their contents liquid; some have facilities for nitrogen blanketing, necessary, for example, in the case of phenol that turns pink when exposed to air and light. Most tank bottoms slope toward a “deepwell plug,” which permits the sucking out of the last traces of liquid, leaving only the “clingage” as a film on the tank wall.

Figure 3.12 illustrates the 171 meter, 30,000 metric ton DWT *Roland Essberger*, a parcel tanker built in 1971.¹³ Such ships might contain 20–30 different chemicals. This one has nine central tanks of capacity 2184 m³ and another nine side tanks of capacity 1100 m³. The heating capacity of the heating coils is 0.0109 m²/m³ in the central tanks and 0.0164 m²/m³ in the side tanks. Thus the side tanks heat up faster.

In principle, tanks can be cleaned and used for different materials. For example, a tanker might ship chemicals to Malaysia and return to Rotterdam carrying palm oil. This, of course, is subject to regulations about contamination. An alternative is for a ship to deliver chemicals to, say, India and return with a cargo picked up at a different location, for example, methanol from the Gulf. A typical cargo load for one of the base routes (such as Rotterdam–India) is shown in Table 3.1.

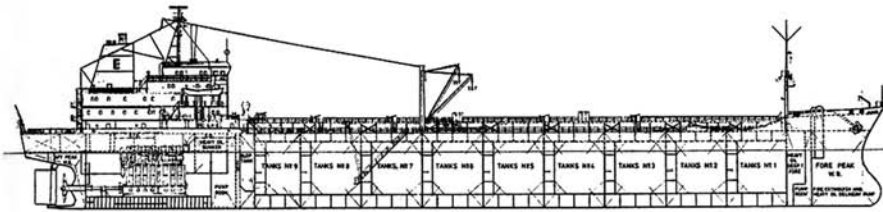


FIGURE 3.12 Parcel tanker TMS *Roland Essberger*. (Courtesy of John T. Essberger Group of Companies.)

TABLE 3.1 A Typical Cargo Load for One of the Base Routes (such as Rotterdam–India)

8000 metric tons ethylene dichloride (for a PVC producer)
4000 metric tons benzene (to cover a shortage locally)
2000 metric tons toluene (for distribution)
2000 metric tons acetone (for solvent distribution or a methyl methacrylate producer)
3000 metric tons <i>o</i> -xylene (for a phthalic anhydride producer)
3000 metric tons <i>p</i> -xylene (for a terephthalic acid producer)
1000 metric tons methyl ethyl ketone (for solvents)
1000 metric tons isopropanol (for solvents)
Perhaps 10 × 500 metric tons other minor solvents (methyl isobutyl ketone, chlorinated compounds, glycol ethers, etc.)
3000 metric tons lubes basestocks
1000 metric tons polyols
1000 metric tons toluene diisocyanate

Note: Together these would fill up a ~35,000 metric tons DWT deep sea tanker such as those in the Stolt Nielsen and Odfjell fleets.

Other commonly shipped organic chemicals are acetic acid, acrylates, epichlorohydrin, ethanol, glycols, methanol, olefins, paraffins, phenol, styrene monomer, and vegetable oils.

Smaller tankers (DWT 2000–10,000 metric tons) tend to cover shorter routes (inter North Sea routes, continental Europe to Scandinavia, north European ports to Mediterranean, Caribbean to U.S. Gulf, Caribbean–U.S. Gulf inter Asian routes, etc.).

3.3.3 Solids

About 90% of global trade is moved by sea and the great container terminal ports around the world control the global supply chain. Traditionally, goods were shipped as break bulk cargo or general cargo, and items were loaded and unloaded individually. Since the late 1960s, this has largely been replaced by containerization. A typical container has doors fitted at one end and is constructed of corrugated weathering steel. Containers were originally 2.44 m (8 feet) wide by 2.44 m high and either a nominal 6.1 m (20 feet) or a nominal 12.2 m (40 feet) long. They can be stacked up to seven units high.

Taller units have been introduced including “hi-cube” or “high-cube” units at 2.9 m (9 feet 6 inches) and 3.2 m (10 feet 6 inches). The United States often uses longer units at 14.63 m (48 feet) and 16.15 m (53 feet). Each container is allocated a standardized ISO 6346 reporting mark (ownership code) four characters long ending in the letter U, followed by six numbers and a check digit. A check digit is the last digit of a bar code designed to be read by computer. It is chosen so that all the numbers in the code add up to a preset number, say, 7, and a single error in transcription is detectable because the total is wrong.

Container volumes are expected to rise in the long term and perhaps to outstrip the ability of some ports to cope, but in the short term the global recession has caused a dramatic drop in business.

It is frequently too expensive to ship an empty container back to its point of origin, so there are thousands of them sitting in docks around the world. Costing about \$2500 new, these abandoned containers can often be bought for as little as \$900, and they are strong and stackable. Put in a window and door, and you have a home; stack a second one on top with a ladder and you have a two room apartment. The Dordoy Bazaar in Bishkek, Kyrgyzstan, is one of Asia's largest markets. It stretches for over a kilometer and is constructed almost entirely from shipping containers stacked two high. And in the developed world, the Travelodge hotel chain opened a 120-room hotel in Uxbridge, United Kingdom, in August 2008, constructed from modified containers. The prefabricated rooms enabled rapid construction on a site with highly restricted access.

Wherever possible, solids' handling of chemicals is avoided. Phthalic anhydride is heated so it can be handled molten; sodium hydroxide is usually distributed as a 50% solution. Solids present unique handling problems. Pneumatic conveyors are the optimum solution. The solid is "vacuumed" from where it is being stored and transferred to another container. Air velocities of 2900 ft/min (14.5 m/s) are needed to convey solids of bulk density 10 lb/cu ft (160 g/liter) rising to 10,500 ft/min (52.5 m/s) for 120 lb/cu ft (1926 g/liter). Variants of the fluidizing system may be used. On a smaller scale, polymer resins are frequently packed in 25 or 1000 kg bags and loaded onto pallets.

3.4 HEALTH AND SAFETY

Chemicals may present a variety of hazards. For example, they may be corrosive, flammable, combustible, poisonous, explosive, or radioactive. They are classified by the International Maritime Organization as IMO1, IMO2, and IMO3 depending on the level of danger they offer. IMO1 is the most hazardous, for example, toluene diisocyanate and acrylonitrile. The IMO2 classification is for less hazardous chemicals and (reclassified a few years ago¹⁴) vegetable oils. The IMO3 classification is for low-hazard chemicals such as hydrocarbons, OXO alcohols, and plasticizers. For the record, IMO0 is wine, fruit juices, mineral oils, and nonhazardous oils; IMO5 is gases, including propane–butane refrigerants; and IMO7 is cryogenic gases, including LNG.

The arrangements made to carry chemicals by sea are regularly inspected to ensure as far as possible that no accidents occur. The procedure is known as ship vetting. It falls into three categories governed by Joint Industry Developed Standards:

1. Ironware (check metalwork on the ship). Is the construction in good condition? Are the electrical systems, pumps, and other key equipment in good order? Are they satisfactory?
2. Crew competence—safe working practices and understanding of safety procedures.
3. Head office safety culture.

Not all countries subscribe to the IMO standards, and countries that are signatories can hold ships that berth in them until they meet the required standards. On the other hand, shipments between countries that have not signed up are unregulated.

Standards and systems of labeling for chemicals are laid down in the United States by the Occupational Safety and Health Administration (OSHA) and in Europe by the EU-OSHA, the European organization for health and safety at work. OSHA requires that all hazardous chemicals be labeled with the known immediate and delayed hazards and that each label contain the following information:

- Identity of the material
- Name and address of a responsible person from whom information can be obtained if necessary
- Precautionary hazard warnings

In addition, the American National Standard Institute (ANSI) has published a voluntary labeling standard (ANSI Z129.1-1988) followed by most chemical manufacturers. This standard calls for the additional following items:

- Signal words—DANGER, WARNING, CAUTION
- Highly toxic materials to be marked POISON
- Precautionary measures useful in preventing physical harm to the individual
- Instructions in case of exposure
- Notes to physician for emergency treatment
- Instructions in case of fire or chemical spill
- Instructions for chemical handling and storage

Other labeling requirements govern the use of simple English, color coding, and so on.

3.5 ECONOMIC ASPECTS

Choice of transport is a compromise between cost, frequency of service, and safety facilities, especially at what may be primitive receiving facilities. Negotiations between merchants and sea captains were traditionally carried out face-to-face at the so-called Baltic Exchange. This has now become an electronically based market, but it retains its name. Bulk freight is concluded between shipowners and charterers via brokers, and similar arrangements are pursued between shippers of solid goods via freight forwarders with container shipping services.

Shipping prices for solids are reflected in the Baltic Dry Index, which is a composite index of shipping prices around the world for dry bulk products such as grain, iron ore, and coal, though not oil. The index for container freight is the Harpex Index, and it covers a much wider range of goods than the Baltic Index. Chemicals spot rates are separate from those for goods generally.

At times of global economic downturn, shipping companies are compelled to reduce their charges to ensure that they obtain whatever trade is going. The reverse applies in boom times. Thus distributors were badly hit by the 2008–2009 recession, and they reduced capacity. The market bounced back in 2010 and took the distributors by surprise, so that capacity was tight for some time. When competition gets more intense, distributors add more technical service elements to their offerings and introduce more packaging, blending, and formulating activities, to assist their principals and meet customer requirements.¹⁵ Shipping companies are more susceptible to pressure than most other branches of the chemical industry; hence the Baltic Dry Index is a key indicator of world trade. On 20 May 2008, at the height of the boom, it reached 11,793; by 5 December, it had plunged by 94% to 663. A normal sort of level is around 2000. In the early 2000s, several of the largest deep sea operators were implicated, both in the United States and Europe, of forming a price fixing cartel. Heavy fines and prison terms were imposed.

Chemicals spot rates depend on the regions between which chemicals have to be moved¹. Rotterdam–Far East and U.S. Gulf–Far East rates have been fairly stable and, between November 2005 and November 2010, have remained between \$70 and \$100/metric ton. Rates between Ulsan (Korea) and the U.S. Gulf or Rotterdam were steady at \$70–80/metric ton between 2006 and July 2008, then shot up to \$118/metric ton and then plunged to \$50/metric ton. The other popular routes are U.S. Gulf–Santos (Brazil), Rotterdam–U.S. Gulf, U.S. Gulf–East Coast Mexico, and U.S. Gulf–Rotterdam. The rates for these shorter journeys have varied between \$30 and \$60/metric ton between November 2005 and November 2010.¹⁶

Many major chemical producers and traders have long term contracts for freight carriage and, even when they don't, there are the spot freight markets that follow the usual supply/demand rules. The shipping trade is fragmented, and a company can exit the business without long term disruption.

3.6 TRADE IN SPECIFIC CHEMICALS

The statistics given above are heavily aggregated and give no indication of what chemicals are being traded. Table 3.2 provides data on the global balance of trade in five different geographic regions in 12 basic organic chemicals in 1997 and 2009. The data for each chemical do not add up to zero, as they should if every world region was taken into account. There are always additional sources of error such as the fact that nations such as Belgium, Hong Kong, Ireland, and Singapore serve as an entrepôt, and, because of re-exports, they often export more than their total chemical production. The balance of trade is a better measure of actual production for export.

The following points emerge from the data:

1. International trade more than doubled between 1997 and 2009, a consequence (or cause or symptom?) of globalization.

TABLE 3.2 Balance of Trade in Specific Chemicals, 1997 and 2009
(thousands metric tons)

1997					
Chemical	Asia-Pacific	Middle East	North America	South America	Western Europe
Acrylic acid	58.00	0.00	-40.00	-7.00	80.00
Acrylonitrile	-618.00	-127.00	789.00	-44.00	-68.00
Benzene	-95.00	83.00	-235.00	254.00	-417.00
Ethylene	-242.00	319.00	219.00	-44.00	-256.00
Ethylene glycol	-2715.00	1255.00	1096.00	18.00	-242.00
Polyethylene	-2054.00	928.00	2266.00	-1111.00	223.00
Polypropylene	-27.00	-460.00	335.00	-125.00	430.00
Propylene	-69.00	164.00	97.00	121.00	-78.00
Propylene oxide	-164.00	-18.00	87.00	-17.00	3.00
<i>p</i> -Xylene	-95.00	83.00	351.00	-5.00	-129.00
Styrene	-369.00	215.00	698.00	-242.00	-233.00
Vinyl chloride	-806.00	13.00	685.00	-170.00	-95.00
Grand Total	-7196.00	2455.00	6348.00	-1372.00	-782.00
2009					
Chemical	Asia-Pacific	Middle East	North America	South America	Western Europe
Acrylic acid	79	0	6	-44	3
Acrylonitrile	-572	-191	484	0	141
Benzene	956	194	-1144	125	-553
Ethylene	-475	1145	88	-59	-600
Ethylene glycol	-6156	5097	1615	-117	-307
Polyethylene	-4952	5254	1171	-502	-345
Polypropylene	-1923	1460	817	63	540
Propylene	-654	375	315	-97	138
Propylene oxide	-180	61	119	-31	5
<i>p</i> -Xylene	-1347	1425	223	-39	-372
Styrene	-1559	1452	795	-363	-36
Vinyl chloride	-599	267	721	-327	-170
Grand Total	-17382	16539	5210	-1391	-1556

Note: Negative trade balances have minus signs.

Source: Based on Nexant Inc.

2. In spite of the growth in indigenous chemicals production, Asia-Pacific was still a huge net importer of basic organic chemicals, 2009 imports being almost two and a half times as great as 1997. The most conspicuous imports were polyethylene as a general purpose plastic and ethylene glycol/*p*-xylene as raw materials for polyester fibers.
3. The Middle East positive balance of trade has mushroomed almost sevenfold. It is no longer a net importer of polypropylene and, indeed, exports large

quantities. Its production of polyethylene and ethylene glycol/*p*-xylene approximately mirrors Asia-Pacific's imports.

4. North America remains an important exporter, but its share of global trade has decreased. It has a negative balance of trade only in acrylic acid, which is scarcely important, and benzene, which it always lacks because it does not crack naphtha to give pyrolysis gasoline. Ethylene glycol and polyethylene remain major exports but only the glycol shows a healthy balance, the polyethylene balance having halved.
5. Ethylene and propylene are not shipped on a large scale, because transportation of gases is expensive, but Europe has a surprisingly unfavorable balance. The Middle East trade balance in ethylene has almost quadrupled since 1997, but propylene has only doubled, reflecting that the Saudis crack ethane but not propane and butane.
6. South America is not a major player and the total of its trade balances has remained relatively small, static, and negative.
7. Western Europe, which has a positive overall chemicals balance of trade, is a net importer of seven of the twelve organic chemicals in our list, one fewer than in 1997. The balances for propylene and acrylonitrile have gone from negative to positive, and the reverse has occurred for polyethylene. Benzene and *p*-xylene, surprisingly in view of the pyrolysis gas situation, have less favorable balance. Only polypropylene shows any signs of flourishing.

The above discussion shows how complex chemical markets are. On an overall basis, the North American and European positions are still strong but their position is being eroded. Asia-Pacific is a huge consumer, but many of the chemicals they import are re-exported as textiles or children's toys. How fast vertical integration with the newly planned chemical plants will proceed is open to debate, as is the effect of shale gas on the competitiveness of the North American industry.

3.7 TOP SHIPPING COMPANIES

The names of the top chemical companies will be familiar to anyone with a chemical background. This need not be true for shipping companies, and the following is a brief selection of shipping companies. Details of them can be found on their websites.

There are about 10 major/minor operators handling large ocean tankers with DWT above 20 kt. The largest are Stolt Nielsen (www.stoltnielsen.com) and Odfjell (www.odfjell.com). These websites show their worldwide trade routes, tonnage transported, fleet data, and details of their ships. Other major deep sea chemical tanker operators are MISC (Malaysian International Shipping Corporation), JO Tankers, and Tokyo Marine. Operators handling smaller tankers with DWT 2000–10000 metric tons include Essberger (www.essberger.de) and Crystal Pool (www.crystal.fi).

Probably the largest operator dealing with rail transport is the German company VTG (www.vtg.de). Road transport is handled by Suttons (www.suttonsgroup.com), whose website has useful details of isotanks. For bulk chemical land based storage log onto www.vopak.com.

ENDNOTES

1. We are indebted to Dr Michael Derenberg for discussions on the transportation of chemicals, and to Jan Fraser-Jenkins for information on rates.
2. DWT (d.w.t. or, D.W.T., dwt) is the so-called deadweight tonnage and is a measure of how much weight a ship is carrying or can safely carry. It is the sum of the weights of cargo, fuel, fresh water, ballast water, provisions, passengers, and crew.
3. Some basic information can be viewed by googling “ARG ethylene pipeline” for the gas section. ARG has data on pipeline costs versus overland/seaborne costs.
4. <http://www.eia.doe.gov/emeu/security/oilflow2.gif>.
5. *Piracy in the Strait of Malacca*, <http://en.wikipedia.org>.
6. J. Bahadur, *Deadly Waters: Inside the Hidden World of Somalia's Pirates*, London: Profile, 2011.
7. F. Gibb, *London Times*, 7 April 2011.
8. British Petroleum Company, *Our Industry—Petroleum*, 5th ed., 1977, is practically an antique but still contains useful information and is available through Amazon.
9. http://en.wikipedia.org/wiki/LNG_carrier.
10. http://www.theodora.com/pipelines/world_oil_gas_and_products_pipelines.html.
11. <http://bluebox.bohmann.at/24/downloads/download4578.pdf>.
12. www.stoltnielsen.com
13. We are indebted to Essberger (www.essberger.de) for this illustration.
14. Fred Doll, *Oils and Fats International*, July 2007, 26,29,30.
15. ICIS.com 3 June 2011.
16. SSY Consultancy and Research Ltd, January 2011.

CHAPTER 4

Chemicals from Natural Gas and Petroleum

Where do industrial organic chemicals come from? Table 4.1 provides a guide. Natural gas and petroleum are the main sources. From them come seven chemical building blocks on which a vast organic chemical industry is based. These are ethylene, propylene, the C₄ olefins (butenes and butadiene), benzene, toluene, the xylenes (*ortho*, *meta*, and *para*), and methane. The olefins – ethylene, propylene, and butadiene and the butenes – are derived from both natural gas and petroleum. The aromatics, benzene, toluene, and xylenes, are derived from petroleum and to a very small extent from coal. Methane comes from natural gas.

Whether natural gas fractions or petroleum is used for olefins varies throughout the world depending on the availability of natural gas and the demand for gasoline. Both light and heavy naphthas (see Table 4.2) are petroleum fractions that can be cracked to make olefins. They can also be used for gasoline. In the United States demand for gasoline is higher than for other petroleum fractions. Consequently, the price of naphtha has traditionally been high and the chemical industry has preferred to extract ethane and propane for cracking to olefins from what has hitherto been abundant natural gas. This is dictated by linear programming techniques that define the appropriate mix of feeds to maximize profitability in the flexible crackers in the United States. It is, of course, also influenced by the gas price. Starting at \$2 per million BTU at the beginning of 2000, it rose to \$10 at the beginning of 2001, dropped to \$2 again at the beginning of 2002, rose to \$15 at the end of 2005, back to \$7 in 2007, and back up to \$13 in mid-2008. These fluctuations severely disturbed steam cracker economics. The 2008 peak was followed by a precipitous drop (Section 4.2).

The United States has traditionally been an important exporter of ethylene derivatives because of the availability of cheap gas. By 2008 it was felt that U.S. gas would never again be cheap enough to compete in international derivatives' trade

TABLE 4.1 Sources of Organic Chemicals

Natural gas and petroleum
Ethylene (Chapter 5)
Propylene (Chapter 6)
Butenes and butadiene (Chapter 7)
Benzene (Chapter 9)
Toluene (Chapter 10)
Xylenes (Chapter 11)
Methane (Chapter 12)
Coal (Chapter 14)
Synthesis gas (CO and H ₂) (see also Chapter 12)
Acetylene ^a
Fats and oils (Chapter 15)
Fatty Acids and derivatives
Carbohydrates (Chapter 16)
Cellulose
Starch
Sugars
“Gums”

^a Although coal is the traditional source of acetylene, much of it is currently produced either from methane or as a by-product in ethylene production (Section 12.3).

with the cheap gas of the Middle East and of other parts of the world. The discovery of a way to mine shale gas has restored the hope that the United States might once again obtain an important share of the ethylene derivatives business.

In Western Europe and Japan the demand for gasoline is lower because on a *per capita* basis there are half as many cars as in the United States, and they are smaller and are driven shorter distances. Thus in Western Europe more naphtha is produced than is required for gasoline. Also, natural gas is less abundant and contains less ethane. Consequently, naphtha has been the important European raw material for the manufacture of olefins. This is equally true in Japan, which lacks resources of either natural gas or oil. In the late 1990s and 2000s naphtha has been a more attractive feedstock because it produces more propylene than does ethane or propane (see Table 4.6) to help assuage the propylene shortage. On the other hand, the rise in oil price has diminished its appeal.

Figure 4.1 illustrates the difference in demand for refinery products in the United States, Western Europe, Japan, and China. The trend across the board is the diminution in the use of fuel oil at the expense of middle distillates, reflecting the replacement of fuel oil by natural gas, which did not come on stream on a large scale outside the United States until the 1970s. For almost twenty years, gasoline represented about 42% of the US oil barrel, up from 40% in the late 1960s, but it has since risen to about 50% presumably because of a rise in the number of vehicles. In Western Europe, the proportion of the barrel going into gasoline has remained steady. In Japan, gasoline and middle distillates have both gained at the expense of fuel oil, so that the

TABLE 4.2 Crude Oil Distillation

Fraction	Boiling Point Range	Comments
Gases		
Methane (65–90%), ethane, propane, butane	Below 20°C	Similar to natural gas. Useful for fuel and chemicals. Also obtained from catalytic cracking and catalytic reforming. Some of it is flared because of cost of recovery. <i>n</i> -Butane, however, is practically always recovered.
Naphtha		
Light naphtha (C ₅ ,C ₆ hydrocarbons)	70–140°C	Naphtha is predominantly C ₅ –C ₉ aliphatic and cycloaliphatic compounds. May contain some aromatics. Base for gasoline. Useful for both fuel and chemicals. Light naphtha is now considered undesirable for gasoline because catalytic reforming yields benzene, which is toxic and has a relatively low octane number.
Heavy naphtha (C ₇ –C ₉ hydrocarbons)	140–200°C	
Atmospheric gas oil		
Kerosene	175–275°C	Contains C ₉ –C ₁₆ compounds useful for jet, tractor, and heating fuel.
Diesel fuel	200–370°C	Contains C ₁₅ –C ₂₅ compounds, mostly linear. Useful for diesel and heating fuels. Gas oil is catalytically cracked to naphtha and may be steam cracked to olefins.
Heavy fractions		
Lubricating oil	Above 370°C	Used for lubrication
Residual or heavy fuel oil	Above 370°C	Used for boiler fuel. Vacuum distillation gives vacuum gas oil for catalytic cracking.
Asphalt or “resid”		Used for paving, coating, and structural applications.

Japanese and, indeed, the Chinese are both using a higher proportion of gasoline than the Europeans.

What was once a straightforward raw material supply situation has become complicated by the discovery of natural gas in many parts of the world in the 1970s. Dramatic discoveries in Siberia mean that the CIS possesses a quarter of the world's natural gas reserves. Gas fields have also been discovered in Qatar, Canada, New Zealand, the Arabian Peninsula, Malaysia, Trinidad, and North Africa. In

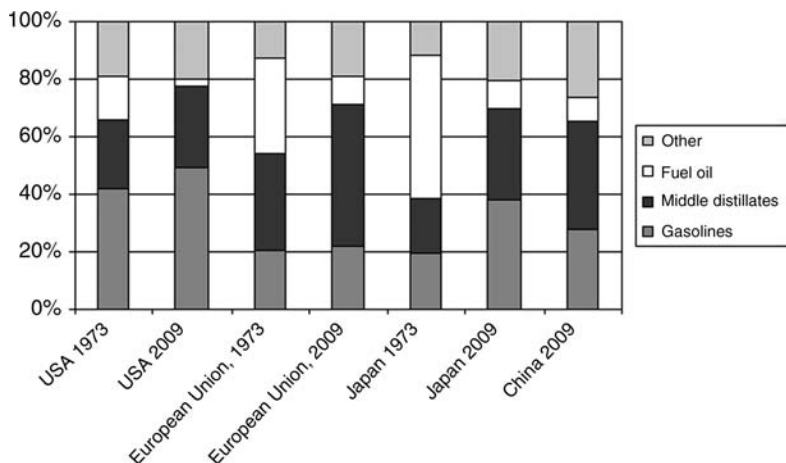


FIGURE 4.1 Patterns of oil consumption. Middle distillates = kerosenes and gas and diesel oils; fuel oil includes bunker crude for ships; other = refinery gas, LPG, solvents, petroleum coke, lubricants, bitumen, wax, refinery fuel, and losses. (Source: BP Statistical Review of World Energy.)

Venezuela and the Middle East, particularly Saudi Arabia, large quantities of associated gas (the gas that accompanies oil deposits as opposed to that occurring in separate gas fields) are available. In many of these countries, particularly Canada and Saudi Arabia, this gas has become the basis for new chemical industries. The economic consequences of these developments will be discussed further in Section 4.5.2.

Probably 95% by weight of the organic chemicals the world uses comes from petroleum and natural gas, and we therefore devote most of our space to them. In addition, we consider what might happen if petroleum supplies are exhausted in the next 50–60 years. The reserves-to-current production ratio in 2009 was 45.7 years for oil and 62.8 years for gas. These figures have *risen* from 31 and 41 in 1967 so that “peak oil” has not yet been reached, in spite of increasingly gloomy predictions and the certainty that reserves must be finite. On the other hand, huge natural gas deposits were discovered in the 1980s throughout the world, most of them in remote locations. The oil equivalent of these reserves is about four times current petroleum reserves. How to commercialize the so-called remote or stranded gas reserves, when the gas is not readily transportable, is a key problem for the chemical and energy industries (Section 12.7). The ready availability of oil and gas, especially shale gas, clouds the inevitability of future shortages. There is still a need for strategies for the future.

A less important current source of chemicals is coal. Coal was historically important, and much of the progress in the chemical industry until World War II was motivated by the availability of coal. Indeed the famous English chemist, W. H. Perkin, could claim to have founded the organic chemical industry in 1865 when, while trying ineptly to synthesize quinine, he obtained a dye with a mauve color from

coal tar intermediates. So important was Perkin's dye that its color gave its name to a period of history known in literature as the "mauve" decade.

The decline of coal coincided with the rise of petrochemicals. However, reserves of coal are much greater than those of oil. If petroleum becomes scarce, will coal come into its own again? Is it a realistic part of an alternative strategy? The so-called C_1 chemistry (Sections 12.5 and 12.6) that developed in the 1960s and 1970s when petroleum shortages loomed large assumed that it would, if the industry was willing to provide the tremendous capital investment a switchover would require. Recent discoveries of natural gas and methods of extracting it from shale, however, mean that any switchover will be considerably delayed in regions with reasonable access. In China, on the other hand, a coal-based chemical industry is contributing to that country's economic success. World primary energy patterns are changing only slowly. Currently, oil constitutes 35% of global energy consumption, coal 29%, natural gas 24%, nuclear 5.5%, and hydroelectricity 6.6%.

The third and final source of organic chemicals is the group of naturally occurring renewable materials of which triglycerides (fats and oils) and carbohydrates are the most important. Although they account at present for only a few percent by weight of the products of the chemical industry, there has been much discussion of how they might be used to replace non renewable fossil materials (oil, coal, natural gas) if the latter ran out or with the aim of reducing carbon dioxide emissions. We review some of this chemistry also.

The third group includes hundreds of more obscure natural products that make contributions to specialized segments of the chemical industry. Examples of such materials are sterols, alkaloids, phospholipids, rosin, shellac, and gum arabic. Their contribution to the chemical industry in terms of value or weight is small, but they are irreplaceable for products such as certain pharmaceuticals, flavors, and fragrances, whose value is very high.

4.1 PETROLEUM DISTILLATION

To gain an idea of how petroleum is used as a source of chemicals one needs to know what happens in a petroleum refinery. Consider a simple refinery (Table 4.2 and Fig. 4.2) in which crude oil, a sticky, viscous liquid with an unpleasant odor, is separated by distillation into various fractions.

The first most volatile fraction consists of methane and higher alkanes through C_4 and is similar to natural gas. These are dissolved in the petroleum. The methane and ethane can be separated from the higher alkanes, primarily propane and the butanes. The methane/ethane mixture is called "lean gas" from which the ethane can be separated if required. The C_3/C_4 mixture is called liquefied petroleum gas (LPG). It may be used as a petrochemical feedstock or a fuel. These and other fractions from oil and natural gas are known by various abbreviations summarized in Table 4.3. Butane is also separated for use in gasoline for volatility control, although government regulations in the United States have decreased this application because the butane contributes to ozone layer destruction. Butane is used to a lesser extent as a raw

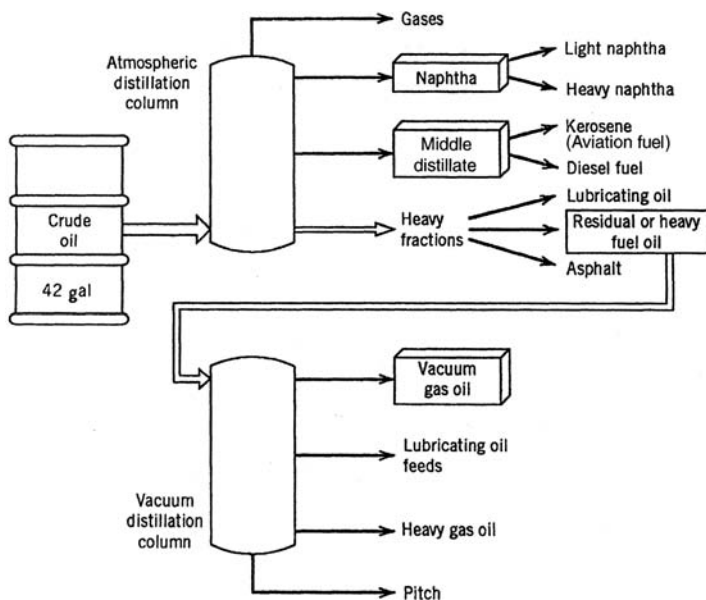


FIGURE 4.2 Crude oil distillation.

material for chemicals (Section 7.4). Some gas contains C_5 , C_6 , and even higher liquids. This mixture is called condensate. It resembles light naphtha (Section 4.5.3) and can be used in similar applications.

In the past, the high cost of compressing or liquefying and shipping these refinery gases has dictated that most of them be flared, contributing to the carbon dioxide burden of the atmosphere. As the price of natural gas increased, however, shipping of methane in refrigerated tankers has become commonplace. Alternatively, methane

TABLE 4.3 Petroleum and Natural Gas Abbreviations

Abbreviation	Meaning	Composition
NG	Natural gas	Methane plus small amounts of ethane and propane
LNG	Liquefied natural gas	Liquid methane
NGL	Natural gas liquids	Ethane and propane condensed from natural gas
Lean gas		Methane and ethane from natural gas
LPG	Liquefied petroleum gas	Liquid propane and butane from associated gas from oil wells
Condensate	A C_5+ fraction from certain oil wells	Similar in composition to light naphtha

may be converted to methanol, which is a useful organic chemical building block (Section 12.5.2) and is more easily shipped. Nonetheless, the World Bank estimates that over 150 billion cubic meters of natural gas are flared or vented annually, an amount worth approximately \$30.6 billion, equivalent to 25% of U.S. gas consumption or 30% of European Union gas consumption per year.¹ The worst offender is Nigeria but some refinery gas is still flared even in the United States.

The second fraction comprises a combination of light naphtha, or straight run gasoline, and heavy naphtha and is of particular importance to the chemical industry. The term naphtha is not well defined, but the material steam cracked (Section 4.5.1) for chemicals generally distills between 70 and 200°C and contains C₅–C₉ hydrocarbons. Naphtha contains aliphatics as well as cycloaliphatic materials such as cyclohexane, methylcyclopentane, and dimethylcyclopentane. Smaller amounts of C₉+ compounds such as polymethylated cycloalkanes, and polynuclear compounds such as methyldecahydronaphthalene may also be present. Like the lower alkanes, naphtha may be steam cracked to low molecular weight olefins. In the United States, its main chemical use is its conversion by a process known as catalytic reforming into benzene, toluene, and xylenes (BTX) (Section 4.8). Catalytic reforming is also a source of aromatics worldwide, although in Western Europe benzene and toluene are mainly derived from pyrolysis gasoline, an aromatics fraction that results from steam cracking of naphtha or gas oil (Section 4.5.1).

Light naphtha, with its octane number raised by addition of lead alkyls, was at one time used directly as gasoline; hence its alternate name, “straight run gasoline.” It contains a high proportion of straight chain hydrocarbons (*n*-alkanes), and these resist oxidation much more than branched chain hydrocarbons (isoalkanes), some of which contain tertiary carbon atoms. Consequently, straight run gasoline has poor ignition characteristics and a low octane number of about 60. It is of little use as gasoline for modern high compression ratio automobile engines, and its properties are even worse if it is unleaded. Isomerization (Section 4.13) of its components to branched compounds increases its octane number and thus its utility. Chemically, however, its significance is like that of naphtha, for it can be cracked to low molecular weight olefins. It does not perform well in catalytic reforming, giving large amounts of cracked products and small amounts of benzene. Benzene is no longer a welcome constituent of gasoline because of its toxicity and relatively low octane number. The situation is summarized in Figure 4.3.

As noted above, international practice has differed. The United States has preferred to crack ethane and propane from natural gas, while the rest of the world has cracked naphtha. The rising price and predicted shortages of natural gas in the United States projected in the 1970s led to an increased interest in liquid feedstock cracking. The preferred liquid feedstock is naphtha, which has traditionally been preempted in the United States for gasoline manufacture. Accordingly, gas oil steam cracking was developed. This was not considered when natural gas was cheap and plentiful, because cracking of gas oil to olefins is accompanied by tar and coke formation. The predicted price rises together with shortages, however, motivated techniques for ameliorating this latter problem, and it is now possible to crack gas oil as well as naphtha. The industry has been loath to do so because it is usually more economic to

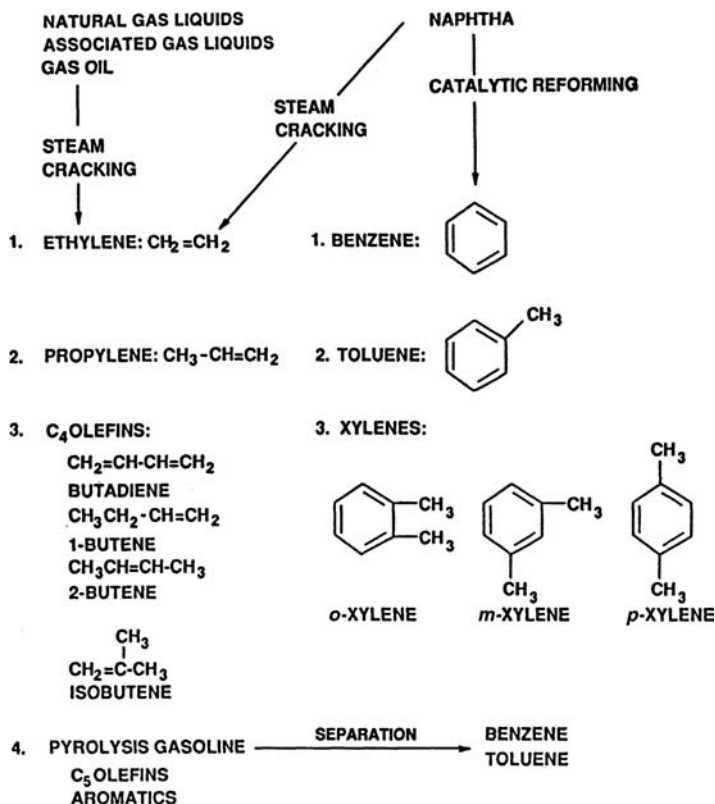


FIGURE 4.3 Steam cracking and catalytic reforming.

crack ethane and propane. They are easier to handle and provide fewer coproducts, and much less coke.

From the 1980s onwards, the switch to liquid feedstocks lost momentum for three reasons. First, natural gas discoveries in Canada meant that cheap natural gas could be imported and in 1999 was about 14% of consumption. Second, Saudi Arabia decided to base its chemical business on the cracking of ethane only, making LPG (propane/butane) mixtures available on the world market. Much of it went to Japan. The third reason was shale gas.

4.2 SHALE GAS

Because of shale gas, U.S. natural gas production was maintained and, indeed, augmented. Reserves were being depleted by the turn of the millennium – the reserves/production ratio was down to 8.8 years in 1999 – but production was scarcely down from the 1973 peak. Disaster threatened, but the “U.S. Cavalry” arrived in time. There was a dramatic improvement in the technology for extracting

shale gas. By 2008 the ratio had risen to 11.6 years and the talk was of proved and potential gas lasting another hundred years! This turnaround was partly due to fresh discoveries, some by “wildcatters” but largely to the exploitation of unconventional gas reserves – from shale, “tight” (low permeability) sands, sandstones and carbonates, coal beds, and ultra-deep (>15,000 feet) reservoirs. Such resources constituted an estimated 47% of natural gas supply in 2007 (6% shale gas, 10% coal bed, 31% tight gas). Price rises stimulated drilling² activity. A high price meant much activity but once new supplies had come on stream, price and activity dropped. The number of active drilling rigs in August 2008 was 770 (in July 2008, the price was >\$13/mmBTU) and the drop to \$3.50/mmBTU in July 2009 was accompanied by a drop in active rigs to 238.^{3,4} In 2000, 1% of U.S. gas came from shale. Estimates in 2008 were that shale gas output would be equal to half of conventional gas by 2020; other estimates are even more optimistic. The U.S. gas reserves, estimated at about 170 trillion m³ (153 trillion metric tons oil equivalent), including 37 trillion m³ (333 trillion metric tons oil equivalent) of shale gas in 2007, have been increased to 1800 trillion (51 trillion m³). The main areas accounting for this increase are in the midcontinent, Gulf Coast, and Rocky Mountain areas. Annual U.S. consumption is about 0.65 trillion m³ (0.585 trillion metric tons oil equivalent).⁵

4.2.1 Shale Gas Technology

Shales are underground rock layers perhaps 60–90 m thick, often found above oil or gas reservoirs. Natural gas occurs within pore spaces and vertical fractures in the shale and adsorbed on organic material. The gas is difficult to extract because the pore spaces are poorly interconnected. Mitchell Energy and Development, a Texas gas producer, solved the problem by a technique called hydrofracturing or fracking.⁶ A hole is drilled vertically into the shale for a distance typically of a mile and then turned horizontally (a technological breakthrough) so that it intersects the vertical fractures. It is lined with a steel pipe. Explosive charges are sent into the horizontal layer to create holes in the pipe walls. Sections of the pipe are sealed and water at high pressure pumped into those areas, fracturing the rock. Release of the pressure would allow the fractures to close again, so a sand-containing gel is pumped in to hold them open. The natural gas can then diffuse through the fractures and be pumped to the surface. Horizontal boreholes of up to 3 km have been drilled.⁷

The downside is that the hydraulic fracturing that releases the gas is expensive; huge amounts of water are required – typically each fracking job uses 15,000 m³ – and this could deplete the water table. There is also the possibility of water contamination from the chemicals that contribute to the success of the operation. The fracking fluid contains 99.75% water and sand. The formulation of the remainder varies between producers but typically contains three additional ingredients: polyacrylamide, a friction reducer; a low concentration biocide; and weak hydrochloric acid. The biocide needs to be used only if the domestic water is not pure enough. The acid will be used, if needed, to help open the perforations to initiate fluid injection.⁸

Between 20% and 90% of the water stays in the well, and what comes back up contains brine and chemicals and may even have radioactive contamination from

natural underground radon. It is stored in open pits until it can be treated. The depletion of the water table is another possibility and, worse, water from the hydraulic fracturing might find its way into the drinking water. There are current complaints from Colorado and Wyoming of tainted groundwater, and vigorous denials from the industry. The regulation of the fracking industry is currently a priority with the EPA. Recent reports are that groundwater is not being contaminated with “chemicals” but with methane, and there are stories of tap water catching fire.⁹ Little is known about the toxicology of dissolved methane.

There is thus a question of the long-term viability of the technique, and also of how far it might be applicable in Europe, where the higher population density means that the large amount of space required for shale drilling is not readily available. The French Senate has voted to ban it. Furthermore, the U.S. glut of shale gas has meant that the \$1.5 billion LNG terminal at the Sabine Pass on the Texas–Louisiana border has been largely unused, and the price of natural gas has remained stable even when the oil price doubled. The Sabine Pass terminal was the world’s largest regasification plant. Gazprom has also postponed its project to develop the giant Shtokman field.

4.3 NAPHTHA VERSUS GASEOUS FEEDSTOCKS

The proportion of C_2+ compounds in shale gas is similar to that in U.S. natural gas and may be extracted in the same way. Figure 4.4 shows the mix of feedstocks used around the world. In the 1980s, The United States cracked only 20% naphtha and 80% ethane/propane. The sharp rise in U.S. gas prices in 2000 (up to \$10/million BTU from a typical value of \$2.50) led to the closure of 30% of U.S. crackers and was expected to lead to a switch to naphtha but this did not occur. Naphtha was too expensive, and there was a shortage. Thus the percentage of gaseous feed cracked in the United States has decreased to 70%, much less than predicted. Figure 4.4 shows the 2008 situation worldwide.

In 1982 Western Europe cracked 90% naphtha and 10% ethane/propane/butane/crude C_4 streams. Because of availability of gas from the North Sea, the percentage of gas cracked in Western Europe doubled by 1995, and by 2008 the nonnaphtha feedstocks in Europe had risen to 30%. Even so the predominant feedstock in Europe will continue to be naphtha. Much North Sea gas lacks the vital ethane and propane; hence gaseous feedstocks are not readily available, even though the crackers could be modified to use them.

The situation in Japan approximates that in Western Europe except that even less gaseous feed is cracked and what is cracked comprises almost entirely butane. The liquid feed is entirely imported naphtha, and it is not expected that gas oil will be cracked in the foreseeable future. On a world basis, 44% of ethylene comes from naphtha, the crackers of gas apart from the United States being in the Middle East and Africa (Nigeria and Algeria), where associated gas is available.

Three decades ago, the United States, Western Europe, and Japan were the only serious players in the ethylene market. By the mid-1980s, however, the impact of the production of ethylene in other parts of the world, primarily the Middle East and

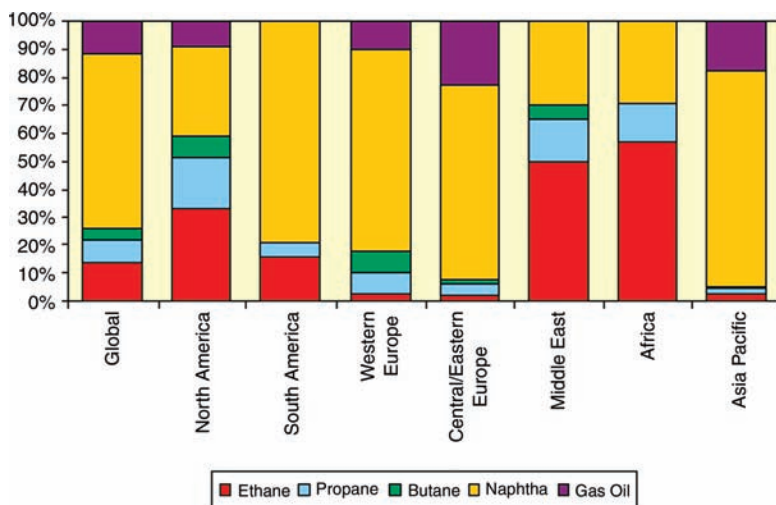


FIGURE 4.4 Cracker feedstocks in various regions (2008). (*Source:* Nexant Inc.)

Canada, was being felt, and these two giants have been joined by many Asian, South and Central American, and Eastern European countries (Section 2.4).

To summarize, the two reactions in Figure 4.3 – steam cracking and catalytic reforming – are the basis for much of the world’s petrochemical production, valued in 2008 at about \$1.2 trillion. The three main raw materials are ethylene, propylene, and benzene, while the C₄ olefins, methane, toluene, and the xylenes are important but to a lesser degree. Methane is an important source of the fertilizer, ammonia, as well as of organic chemicals, primarily methanol. Its most important reaction is the formation of synthesis gas (Section 12.5), from which ammonia and methanol are made. In principle, naphtha may also be used for this (Section 12.4) although it seldom is.

4.4 HEAVIER OIL FRACTIONS

Figure 4.2 indicates that kerosene is a fuel for jet aircraft, tractors, and for domestic heating and has some applications as a solvent. Gas oil is further refined into diesel fuel and light fuel oil of low viscosity for domestic use. Its use as feed for cracking units for olefin production has already been mentioned. Both the kerosene and gas oil fractions may be catalytically cracked to gasoline range materials (Section 4.6). Actually the term gas oil is applied to two types of material, both useful for catalytic cracking. One is so-called atmospheric gas oil, which, as its name indicates, is produced by atmospheric pressure distillation. The other is vacuum gas oil, which results from the vacuum distillation of residual oil from the heavy fraction. It has a much higher boiling range of 430–530°C.

Residual oil (Fig. 4.2) boils above 350°C. It contains the less volatile hydrocarbons together with asphalts and other tars. Most of this is sold cheaply as a high viscosity

TABLE 4.4 Value of Various Oil Fractions

Product	Typical Ratio of Value of Product to Cost of Crude Oil in the United States ^a
LPG	1.1–1.4
Motor gasoline	1.4–1.5
Naphtha	1.2–1.3
Gas oils	1.15–1.3
Jet kerosene	1.3–1.4
Vacuum gas oil	0.95–1.05
Heavy fuel oil	0.6–0.7

^a European figures are similar but gas oil prices tend toward the top of the range and naphtha/motor gasoline toward the bottom.

heavy fuel oil (bunker oil), which must be burned with the aid of special atomizers. It is used chiefly on ships and in industrial furnaces.

A proportion of the residual oil is vacuum distilled at 0.07 bar to give, in addition to gas oil as mentioned above, fuel oil (b.p. <350°C), wax distillate (350–560°C), and cylinder stock (>560°C). The cylinder stock is separated into asphalts and a hydrocarbon oil by solvent extraction with liquid propane in which asphalts are insoluble. The oil is blended with the wax distillate, and the blend is mixed with toluene and methyl ethyl ketone and cooled to –5°C to precipitate “slack wax,” which is removed by filtration. The dewaxed oils are purified by countercurrent extraction with such solvents as furfural, which remove heavy aromatics and other undesirable constituents. The oils are then decolorized with Fuller’s Earth or bauxite and are blended to give lubricants.

Part of the vacuum distillate and the “slack wax” can be further purified to give paraffin and microcrystalline waxes used for candles and the impregnation of paper. The petroleum industry is constantly trying to find methods by which the less valuable higher fractions from petroleum distillation can be turned into gasoline or petrochemicals. Table 4.4 gives an indication of the values of the various fractions relative to the cost of crude oil.

4.5 STEAM CRACKING AND PETROLEUM REFINING REACTIONS

The production of chemical feedstocks from petroleum is inextricably associated with the production of gasoline and other fuels. Sometimes these two industries compete for raw materials, and sometimes they complement each other. The chemical industry is a junior partner because it consumes only about 6% of refinery output in the United States and rarely more than 8% anywhere else. On the other hand, because it produces premium, higher added-value products, it can compete with other consumers in buying those raw materials it needs. The chemical industry can compete successfully

because the petrochemicals and the industrial and consumer products made from them represent very high “value added” as compared to the value of the starting materials. In order to understand this competition and the operation of a petroleum refinery, we must examine the chemical processes that follow the physical process of distillation.

We have already noted that straight run gasoline has too low an octane number for high compression ratio engines. A major objective of a petroleum refinery is to raise this number. It is achieved by way of the reactions summarized in Table 4.5, most of

TABLE 4.5 Steam Cracking and Petroleum Refining Reactions^a

Cracking

- * **Steam Cracking:** Converts *n*-alkanes, cycloalkanes, and aromatics in oil, or ethane, propane, butane and higher hydrocarbons in natural gas into ethylene, propylene, butenes and butadiene. The products are primarily for the chemical industry. Steam cracking is thus not a petroleum refining reaction but frequently takes place in a refinery.
- * **Catalytic Cracking:** Produces molecules with five to twelve carbon atoms suitable for gasoline from larger molecules. Facilitates formation primarily of branched chain molecules and of some aromatics.
- * **Hydrocracking:** Upgrades heavy crudes by converting them to more volatile products. Uses catalysts together with hydrogen, which prevents “coke” formation on the catalyst and converts objectionable sulfur, nitrogen, and oxygen compounds to volatile H₂S, NH₃, and H₂O.

Polymerization: Combines low molecular weight olefins into gasoline-range molecules known as polygas with H₂SO₄ or H₃PO₄ catalysts. It is not widely used today, but there is renewed interest because, if MTBE is phased out, it can be used to produce isooctene from the surplus isobutene. This can be used as such or hydrogenated to isooctane, which will somewhat enhance octane number in unleaded gasoline. A more appropriate term would be oligomerization, since oligomers, not polymers, are formed.

- * **Alkylation:** Combines an olefin with a paraffin (e.g., propylene with isobutane) to give branched chain molecules. H₂SO₄ and HF are used as catalysts. Very important in achieving high octane number in lead-free gasoline.
- * **Catalytic Reforming:** Dehydrogenates both straight-chain and cyclic aliphatics to aromatics, primarily benzene, toluene, and xylenes (BTX) over platinum–alumina or rhenium–alumina catalysts. Most widely used refinery reaction in the United States.

Dehydrogenation: Cracking and reforming are basically dehydrogenations. Other dehydrogenations include conversion of ethylbenzene to styrene, butenes to butadiene, and propane to propylene.

Isomerization: Used to convert straight-chain to branched chain compounds—for example, *n*-butane to isobutane for alkylation, *n*-pentane to isopentane, and *n*-hexane to isohexane in low boiling naphtha. Other refinery isomerizations include *o*-xylene and *m*-xylene to mixed xylenes (Chapter 9).

Coking: Used to remove metals from a refinery stream. Heat in the absence of air “cracks-off” hydrocarbons. The metals stay behind in the “coke.”

Hydrotreating: Like hydrocracking, converts sulfur, nitrogen, and oxygen in petroleum fractions to the gases, H₂S, NH₃, H₂O. Uses hydrogen from other refining processes such as reforming. Can be applied to heavy feedstocks.

^a Asterisk indicates most important processes.

which either modify a petroleum fraction or provide the raw material for another reaction that will give compounds with an improved octane number. In a modern refinery these reactions as well as distillation take place under computer control. Conditions and output are varied according to the ever-changing demands of the market and the composition of the feedstock, which in turn may vary from day to day and storage tank to storage tank.

Before we consider petroleum refining reactions, however, we shall describe steam cracking. Steam crackers are wholly petrochemicals targeted. About two-thirds of them are built as an add-on to a refinery, as with ExxonMobil and SABIC. This is convenient if the refinery provides the raw materials for steam cracking. The remaining third are at the front end of a petrochemicals plant, as with Dow and BASF. The description here applies to the cracking of naphtha; the cracking of ethane is analogous but much simpler.

4.5.1 Steam Cracking

Steam cracking, derived from the thermal cracking process introduced as early as 1912, involves the use of heat, but no catalyst. William Burton was awarded the 1922 Perkin Medal for his research.¹⁰ The Burton process for cracking was first, but close on its heels was the Dubbs process. Dubbs was so involved with technology that he named his son Carbon and his daughters, Methyl and Ethyl. Carbon later took on the middle name of Petroleum.

From naphtha feedstocks steam cracking yields mainly C_2 , C_3 , and C_4 olefins and an aromatic fraction called pyrolysis gasoline. Because the olefins are not useful in gasoline, it has long since been superseded for gasoline production by catalytic cracking. It is, however, the mainstay of the petrochemical industry. The insignificance of chemicals production compared with that of gasoline is illustrated by the fact that only 9% of total U.S. cracking capacity is steam cracking. The rest is catalytic cracking.

The modern steam cracking process uses light liquid or gaseous feedstocks (Section 4.1), a high temperature (650–900°C), and a low pressure, to maximize the yield of low molecular weight gases. Since it is inconvenient to operate a plant below atmospheric pressure, because a small leak could lead to the formation of explosive hydrocarbon/air mixtures, the partial pressure of reactants is reduced by addition of steam as an inert diluent. The steam also serves to reduce coke formation in the reactor tubes.

The hydrocarbon feedstock is vaporized, if not gaseous to begin with, mixed with steam, and the mixture passed through tubes about an inch (25 mm) in diameter through a furnace heated by oil and gas burners. The residence time is short – 30–100 milliseconds – to minimize coking, which is potentially a major problem since coke and hydrogen are thermodynamically the favored products (Fig. 4.5).

The product gases emerge at about 800°C. As they are to be distilled at low temperatures, they have to be cooled by 900°C with minimum waste of heat – a classic chemical engineering problem. Throughout the process, series of heat exchangers

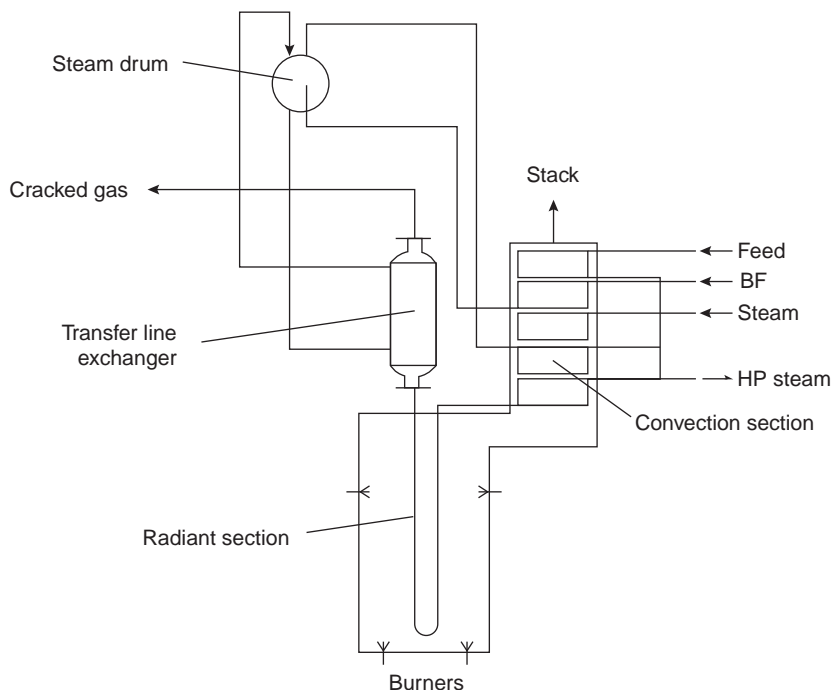


FIGURE 4.5 Typical steam cracking furnace.

conserve the heat used in the early stages and the “coolth” in the later ones. Initially, the gases are quenched to about 400°C in a heat exchanger and the heat used to raise steam to power the turbines of the centrifugal compressors used in the refrigeration process. They are then cooled from 400°C to a little above 100°C in a spray tower cooled by a stream of fuel oil. Additional fuel oil condenses. Some of the fuel oil is removed from the bottom of the spray tower as a product and the remainder cooled and recycled. Further cooling to ambient temperature condenses pyrolysis gasoline plus the steam that was originally added to the feedstock, and these are simply separated in a decanter.

The gases are then scrubbed with ethanolamines (Section 5.11.6.4) to remove acid gases such as carbon dioxide and hydrogen sulfide and dried with molecular sieves. The drying is important, because ice is highly abrasive and would damage the low temperature equipment. The remaining gases are compressed to 40 bar and condensed in a cascade of refrigeration units. Cracking processes only became economically viable because of the development of centrifugal compressors that run the refrigeration processes more cheaply and efficiently than reciprocating compressors. Centrifugal compressors are the greatest contribution of mechanical engineering to the chemical industry. The condensed gases are then distilled in a column called a demethanizer, which carries on top a condenser cooled to -95°C with liquid ethylene.

Methane and hydrogen are the top products, and the C_2+ products emerge as a liquid at the bottom.

This bottom stream is distilled again in a deethanizer in which the C_2 components pass overhead and the C_3 – C_5 hydrocarbons form the bottom product. The C_2 fraction is partially hydrogenated to convert small amounts of acetylene to ethylene. The advantage of carrying out the hydrogenation at such a low temperature is that the acetylenic triple bond is selectively hydrogenated. At higher temperatures, double and triple bonds would be indiscriminately reduced. The importance of removing acetylene is that, when copolymerized with ethylene, it gives a polymer containing double bonds, which cross-link to give a nonlinear product. The ethylene/ethane mixture is distilled to give an ethylene top product that may be further purified to give polymer grade ethylene, and an ethane bottom product that is recycled. (See Figure 4.6.)

A depropanizer column separates the C_3 and C_4 streams, and a debutanizer separates the C_4 s from C_5 s. The latter are combined with the pyrolysis gasoline stream from the first column. The C_3 stream is treated in the same way as the C_2 stream to remove propyne.

4.5.2 Choice of Feedstock

The above basic process may be modified depending on the feedstock. Not surprisingly, the products of steam cracking are affected by this as well as by reaction conditions. Modern crackers operate under severe conditions – high temperatures because fragmentation and dehydrogenation reactions are accompanied by an entropy increase, and low residence times because the equilibrium products are carbon and hydrogen. In the last 35 years, the typical ethylene yield by weight from fairly severe (high temperature) cracking of a naphtha feedstock has been approximately doubled from about 16% to 31%. Higher yields of ethylene have been achieved, but the ready market for propylene means that the anxiety to increase ethylene yields is not as great as it was.

The effect of feedstock is illustrated in Table 4.6. The yield of ethylene decreases and the yields of the coproducts increase as the molecular weight of the feed increases. The economics associated with the use of the different feeds depend crucially on market conditions. Although the cracking of gas has traditionally been the most economical process in the United States, there are times when naphtha cracking is preferred because the coproducts are more profitable. This is particularly true in Europe where a propylene shortage started to develop in the early 1990s and has continued through the 2000s. The United States is isolated from such a shortage by the large amounts of propylene produced in catalytic cracking (Section 4.6). Europe and Japan do not have this reservoir because their lower use of gasoline requires fewer catalytic crackers.

Pyrolysis gasoline is an important product obtained from the cracking of liquids, and the heavier the liquid the more pyrolysis gasoline is produced. It contains aromatics and thus is an important source of benzene and toluene in Europe and Japan. The pattern is shown in Figure 4.7. Much of the toluene converted to benzene

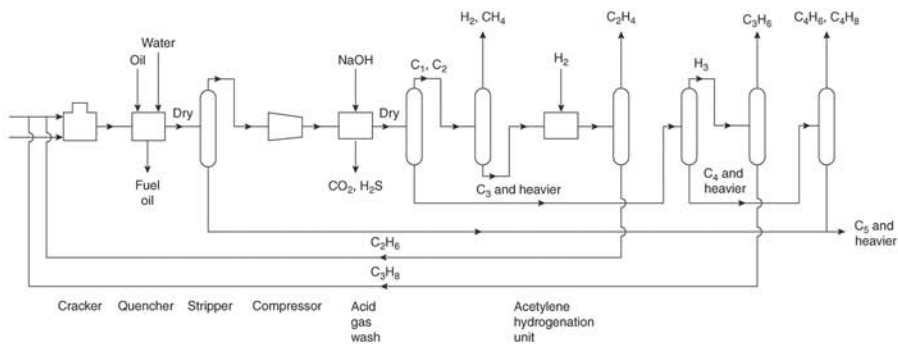


FIGURE 4.6 Simplified flowsheet for a steam naphtha cracker.

TABLE 4.6 Coproduct Yield per 100 kg Ethylene

	Ethane	Propane	Butane	Naphtha	Atmospheric Gas Oil	Vacuum Gas Oil
Feedstock required (lb)	120	240	250	320	380	430
Ethylene (yield %)	80	42	38	31	26	23
Propylene	3	50	40	50	55	60
Butadiene	2	5	9	15	17	17
Other C ₄ olefins	1	3	17	25	18	18
Pyrolysis gasoline	2	15	18	75	70	65
Benzene	1	5	6	15	23	24
Toluene	neg. ^a	neg. ^a	3	10	12	12
C ₅ olefins	neg. ^a	neg. ^a	1	7	8	7
Other	1	10	8	43	37	22
Fuel oil	neg. ^a	2	4	10	70	125
Other ^b	17	65	62	45	50	45

^a Negligible = neg.^b Mainly hydrogen and methane.

also comes from steam cracking. Pyrolysis gasoline is only half as important a source of these chemicals in the United States where catalytic reforming is more widely practiced.

4.5.3 Economics of Steam Cracking

We will now discuss the relative costs of production of ethylene from various feedstocks in various countries.¹¹ The Middle East is the lowest cost producer, the United States comes in the middle, and South Korea and Japan have the highest costs.

The cost of building a plant depends on the chosen feedstock, the degree of flexibility demanded, and the location.¹² In spite of all the engineering ingenuity, elaborate separation processes are costly to build and operate. Ethane crackers, such as those used in Saudi Arabia (Section 4.1), produce so few by-products that separation is simple; naphtha and gas oil crackers are more complicated and consequently more expensive. Crackers are cheapest for light feedstocks. They are smaller per metric ton of ethylene capacity, because they produce fewer coproducts. They also require less elaborate separation processes. Thus the capital cost of a plant to crack various feedstocks increases in the following order: ethane < ethane/propane < light naphtha < full-range naphtha < gas oil. Light naphtha in this context usually means “condensate,” a cheap C₅+ fraction from certain gas wells. It is also called “natural gasoline” and, to add to the confusion, is frequently called simply naphtha. Flexible crackers that can operate on any feedstock are more expensive but involve lower risk. Crackers in developing countries are 10–15% more expensive, in spite of cheap labor, because of the lack of scientific and engineering infrastructure and the

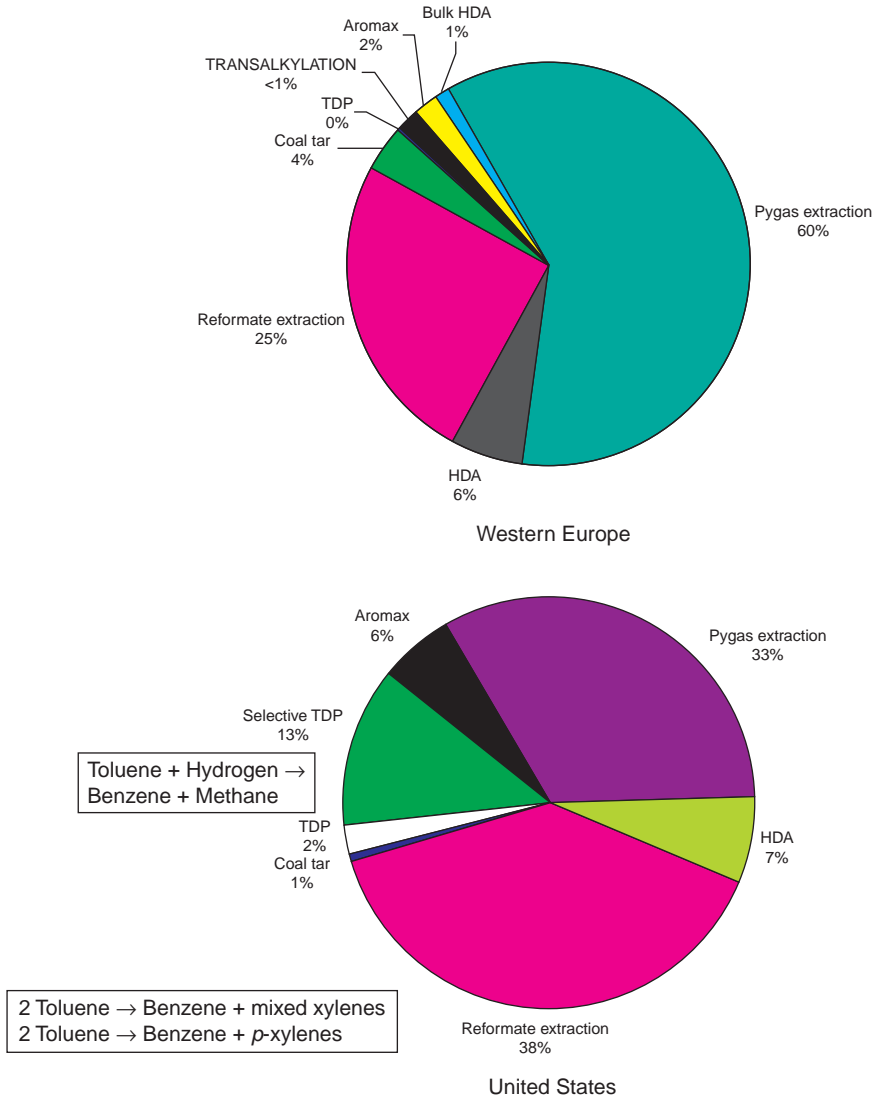


FIGURE 4.7 Sources of benzene in Western Europe and the United States (2009). (Source: Nexant Inc.)

need to import many components. All the same, fixed costs contribute only a few percent to overall costs.

Naphtha is more expensive in the United States than in Europe because of the higher demand for gasoline. The price differential, however, is only about \$15/metric ton because, at a higher price, producers will export material westward across the

Atlantic. When gaseous feedstocks are available, they are usually cheaper per metric ton than naphtha but do not give so many coproducts. Other things being equal, raw material costs are related to the amount of raw material required to produce a metric ton of ethylene. This is higher for naphtha than for gaseous feeds and higher still for gas oil, because they produce more coproducts. Correspondingly, there is more coproduct credit. The coproducts sell at a higher price than the raw materials but at a lower price than ethylene, although propylene sometimes matches it. Depending on the relative prices of the various feedstocks and products, the net raw material price may favor liquid rather than gaseous feedstocks as, for example, when there is a propylene shortage. Nonetheless, even when it exists, this saving is sometimes negated by the higher fixed costs and depreciation.

The flexibility to crack gases or liquids, whichever is more economic and more readily available at a given time, is available to companies who have paid more for their plants. Gaseous feedstocks have traditionally been the more economic. These two factors have accounted for the advantage that the United States, with its historically abundant supplies of natural gas and large supply of refinery propylene, has held in world chemical markets.

The dominance of the United States has been threatened by the entry of Saudi Arabia as a major producer. Ethane is produced there at the wellhead from associated gas and is priced at zero plus the logistic cost of separation and transport, which amounts to about \$38/metric ton (75¢ per million BTUs). The Saudi government wants to diversify its economy and provide employment. It also wants to penetrate world markets and takes the view that the ethane would have to be flared if it were not separated; hence zero wellhead value is acceptable. Indeed, because flaring would cause pollution, one might even maintain that the wellhead value is negative. On the zero value basis, Saudi ethane cracking is much the most economic and sets free for export quantities of propane plus butane (LPG) not required for fuel (Section 4.4). On the other hand, the availability of ethane in Saudi Arabia is limited because it comes from associated gas, the quantity of which is linked to production of crude. Subsequent investment has been based increasingly on the use of condensate and propane. A 30% discount off the lowest export price was granted by the government to producers (and these include non-Saudis) on feedstocks other than ethane.

Gas cracking is more economic when propylene is not in short supply. The United States has taken full advantage of this, importing small amounts of Saudi LPG in addition to its own supplies of ethane/propane and LPG from natural gas. Western Europe cannot take as much advantage of imported LPG because only 5 of the 52 steam crackers that existed at the end of 1993 were truly flexible, and the infrastructure for handling LPG does not exist in Europe to the extent that it does in the United States. Alone among European producers, BASF built port facilities at Antwerp, but the rise in LPG prices meant that they never used them. European natural gas from the North Sea contains little ethane and propane, and only the gas from the northernmost fields provides sufficient of these to be worth cracking. Apart from a small facility operated by Atochem at Lacq in the Pyrenees, France, that has been cracking gas from a small high sulfur deposit of natural gas for over 30 years, the only dedicated gas

cracking units in Western Europe were the Moss Moran cracker and a second train at the BP Grangemouth cracker, both in Scotland. In 2010 BP announced the closure of the Grangemouth cracker.¹³

In addition, Europe is dependent on pyrolysis gasoline for about three-fifths of its benzene and toluene (Fig. 4.7), which gas cracking produces in only small amounts. The toluene is used largely for dealkylation and disproportionation to provide more benzene. Europe's situation is echoed in Japan, Taiwan, and South Korea and is part of the economic structure of their chemical industries. Other Southeast Asian countries are already cracking gases, for example, Malaysia and Thailand, which has a gas cracker alongside two liquid crackers. The key countries likely to crack gas in the future, however, are those of the Middle East – Iran, Kuwait, Abu Dhabi, and Qatar – all of whom are planning facilities in the next few years following the Saudi example. They will aim to export to Europe, while Canada will also crack gas for export to the United States, and Venezuela will export to Central and South America and the United States.

Ethylene from naphtha is economically marginal. Substantial overcapacity in the early 1990s and early 2000s kept prices depressed and forced the sale of surplus product on the spot market. Capacity utilization dropped from 94% in 1989 to 83% in 1993 (see Fig. 2.3). A remarkable sequence of accidents and plant breakdowns in 1994 and early 1995 led to shortages and price rises, and capacity utilization rose to 93%. Prices fell again once repairs had been carried out and by 2002 utilization had dropped to 84% recovering to the nineties in 2004–2008 but dropping again thereafter. Overcapacity seems endemic. The huge new Middle East and Asian capacity threatened from 2010 onwards will exacerbate the situation. Why and how, therefore, do producers based on usually less economic liquid feedstocks keep going? There are four main reasons.

First, many of the crackers in Europe and Japan, as in the United States, are linked into integrated petrochemical complexes. Ethylene is more expensive to ship than to pump over the fence, hence many producers of ethylene derivatives will prefer to draw on their own cracker or a European pipeline to which they are connected rather than to pay for the shipping of ethylene in refrigerated tankers. There is added expense in liquefying the ethylene for shipment and then regasifying it.

Nonetheless, the European pipeline network is much shorter than that in the United States. With an effective pipeline network, fewer crackers are needed and, indeed, the United States has fewer crackers than Western Europe. In 1993, only 63% of European ethylene capacity was connected to a pipeline grid, in contrast to 94% in the United States.

Second, as the European plants are already built, their owners insist on operating them so long as cash costs are covered. Huge new capacity in Europe, planned in the 1980s, came on stream at the start of the 1990s. The plants already operating did not provide sufficient cash flow to justify fresh investment, but the new plants were built on a tide of what in retrospect appears to have been unjustified optimism. The BASF cracker, opened in 1994, was the last European cracker to have been built from scratch. A motivation for building the cracker was cheap LPG available from Saudi Arabia, but by the time the cracker was built the cost of LPG had risen, making it

uneconomical for this use. The European industry association has tried to encourage reductions in capacity but has been largely unsuccessful. Indeed, there have been extensive expansions and debottlenecking exercises, which are relatively inexpensive, and these have kept capacity ahead of demand. Meanwhile, investment costs in developing countries are usually higher than in Europe.

Third, there is the question of tariffs. These are being reduced in the developed world as a result of GATT (General Agreement on Trade and Tariffs) and WTO (World Trade Organization, which replaced GATT in 1995) negotiations, but they remain. Southeast Asia is permitted to protect indigenous manufacturers. In 1995, Chandra Asri started up a 550 thousand metric ton per year naphtha cracker in Indonesia, built there because polyethylene is heavily protected. The Southeast Asian chemical industry relies for its profitability on a local market allied to high tariffs together with exporting to neighboring China.

Further complications arise because of tariffs and transport charges. For example, if South Korea exports propylene to Taiwan, the freight costs are about \$70/metric ton. A costing in Taiwan will include propylene at \$70/metric ton more than a similar costing in South Korea, hence ethylene costs from an identical plant will appear about \$35/metric ton lower. Similarly, a tariff barrier on imported coproducts will raise their value in the importing country and make home-produced ethylene appear cheaper. There is no easy answer to these problems and the reader should treat all costings with circumspection and demand details of all costing conventions before making judgments.

Fourth, the price differential between naphtha relative to gaseous feedstocks has been fluctuating. If the world ethylene market was swamped with material based on ethane, some naphtha-based crackers would have to close. There would then be, indeed there is, a propylene shortage. Prices rise, making the naphtha-based route economic once more.

European producers have survived for the above reasons, but there is no doubt that they have suffered from the new producers around the world and from their misjudgment in building new capacity. ICI, Rhone-Poulenc, and Hoechst decided to leave the heavy chemicals sector. Thus the chemical industries in developed countries are under pressure from those in developing countries. This has everything to do with availability and price of feedstocks, location of plant, and tariffs, and nothing to do with the availability of cheap labor, which makes up a tiny proportion of total costs.

4.6 CATALYTIC CRACKING

Catalytic cracking, as its name implies, fragments molecules over a catalyst. It also dehydrogenates some of them. Typical heavy naphtha and gas oil feedstocks give a mixture of products consisting mainly of isoalkanes suitable for gasoline together with *n*- and isoolefins and *n*-alkanes from C₃ upwards. Little ethylene but significant amounts of propylene and C₄ mono-olefins are produced. Although important to the

gasoline industry, catalytic cracking is not a major route to petrochemicals, except to ensure an ample supply of propylene and butenes for the United States. They are largely used for alkylate for gasoline (Section 4.10).

More propylene is produced by catalytic cracking in the United States than by steam cracking, but it occurs in a more dilute stream and cost is higher. Thus about 55% of refinery propylene is used for chemical production. For the preparation of isopropanol (Section 6.7), cumene (Section 6.6), and oligomers (Section 6.3), it is possible to use refinery grade propylene without upgrading. Also there are legitimate uses for propylene from catalytic cracking in the refinery itself. As indicated above, the two largest are for alkylation (Section 4.10) and directly as fuel. In addition it is mixed in the refinery with LPG and is used for polymer gasoline (Section 4.9). For the C_4 fraction, alkylation with *n*-butenes and isobutene is a major refinery use. Another use is for direct blending of *n*-butane into gasoline, although legislation in the United States now requires that this be eliminated in the summer because volatile butane contributes to ozone layer destruction. A major use for refinery isobutene and isopentene is their reaction with methanol to produce methyl *t*-butyl and, on a smaller scale, methyl *t*-amyl ethers (Section 7.2.1) but this is in decline.

Catalytic cracking received impetus from World War II because military planes required high octane gasoline. At that time, naturally occurring aluminosilicates, primarily amorphous montmorillonites, were used as catalysts. In the mid-1960s synthetic zeolites were introduced. These too are aluminosilicates but with a well-defined crystalline structure. Y zeolites, such as a so-called faujasite with a ratio of silicon to aluminum of 1.5:3.0 and a composition of $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$, are used (Section 18.9). Synthetic zeolites are characterized by the presence of microscopic pores of consistent diameter, and chemical reactions take place inside these pores. The sites within the zeolite that create reactive species include Brønsted sites, Lewis sites, and even superacid sites. It is these that bring about the formation of carbocations, the intermediates that in catalytic cracking lead to the formation of the branched chain compounds, prized because they have a high octane number (see below).

The Y zeolites are modified with rare earths by an ion exchange process. These impart high thermal stability and additional acidity for promotion of chemical reactions. In the early 1990s, catalytic cracking catalysts were announced that increased the isobutene content of the product so that more was available for methyl *t*-butyl ether production. It is now commonplace to add the zeolite ZSM-5 to the catalyst to increase propylene yields and inhibit tar formation.

Catalytic cracking is an excellent example of the important contribution catalysts can make to the improvement of selectivity and yield. In the cracking of gas oil, a conversion of 73% can be obtained with a synthetic zeolite as compared to 64% with a natural silica/alumina.

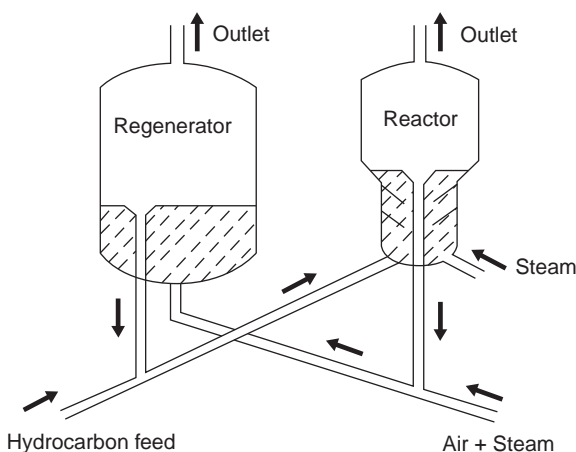
As indicated in Section 4.1, vacuum gas oil is a major feed for catalytic cracking as is atmospheric gas oil. Virtually any petroleum fraction can be cracked, but vacuum gas oil, derived from residual petroleum fractions, has few other uses. Catalytic

TABLE 4.7 Product Mix (approx wt %) from Fluidized Bed Catalytic Cracking of Gas Oil

Propylene	3.2
<i>n</i> -Butenes and isobutene (no butadiene)	5.8
Isobutane	3.3
Branched C ₅ + compounds (gasoline or cat. cracker naphtha)	36.5
C ₁₀ + compounds (gas oil)	15.0
Residue and coke	29.0
Ethylene, ethane, propane, <i>n</i> -butane, H ₂ , H ₂ S	7.2

cracking takes place at a temperature of about 500°C and at atmospheric pressure or slightly above. The reaction is carried out in a fluidized bed reactor in which the finely divided catalyst is maintained in a fluid state by a stream of steam. Residence time is of the order of 1–3 seconds. The products must be rapidly quenched to prevent their decomposition, coke deposits on the catalyst reducing its activity. In its fluidized state, the catalyst can be removed continuously from the reactor as though it were a liquid and is sent to another reactor at 630°C, where the coke is burned off in a stream of air. The regenerated catalyst is then recycled to the fluidized bed. A typical product mix from catalytic cracking is shown in Table 4.7. A diagram of the fluidized bed and regenerator is shown in Figure 4.8.

The search for improved catalysts for catalytic cracking is a vigorous one. The objectives are obvious – to improve yield of branched chain compounds and to decrease the yield of coke, residue, and olefins, except for those useful for alkylation. Zeolite-like materials such as aluminophosphates are reported to offer certain advantages as are zirconium phosphates. These are not true zeolites because they

**FIGURE 4.8** Fluidized bed reactor for catalytic cracking.

have layered rather than crystalline structures, the sites for catalytic reaction being the space between the layers.

4.7 MECHANISMS OF STEAM AND CATALYTIC CRACKING

The overall reactions involved in both thermal and catalytic cracking, with the exception of isomerization, are markedly endothermic but are accompanied by favorable entropy changes. They are therefore both favored by high temperatures and low partial pressures of reactant. The mechanisms and products of the two processes are, however, different. Catalytic cracking involves carbenium ion intermediates, but steam cracking, which is of greater concern to the chemical industry, is a free radical reaction involving the steps illustrated in Figure 4.9, the upper part of which assumes that ethane is being cracked. In the initiation step **(a)** two methyl radicals form. Each of these attacks another molecule of ethane **(b)** to give two molecules of methane plus an ethyl radical. Propagation proceeds as shown in **(c)** and **(d)**. Thus far only ethylene has been produced, and it is indeed the major product of ethane cracking. The termination reaction **(e)** produces *n*-butane by coupling, and this undergoes cracking to yield small amounts of olefins. Also, if ethylene reacts with an ethyl radical, C_4 olefins can be produced by disproportionation **(g)** and, if it reacts with a methyl radical **(h)**, propylene may result. Note that a corresponding amount of alkane is produced, which can undergo further cracking.

When propane is cracked, as in Figure 4.9*(i–m)* much more propylene is produced. This is because propane can be attacked by a hydrogen atom to yield an isopropyl radical **(j)**, which can only convert to propylene. The initial hydrogen atom can come from propane scission **(i)**, which produces a propyl radical. This is in fact a dominant reaction and explains why ethylene is always the major product as in **(l)**. Propyl radicals may also isomerize rapidly **(m)** to give the more stable isopropyl radicals. With butane feedstock or C_4 radicals from other sources such as **(e)**, **(g)**, and **(h)**, rapid isomerization **(n)** can occur. Rearrangement to tertiary butyl radicals is slow. With higher molecular weight feeds, the long chains fragment readily **(m)**, and the preferred reaction of the resulting free radicals is β -scission **(n)** to give ethylene and another free radical. With larger hydrocarbons, rearrangements are also facile, with protons migrating rapidly along the chains, so that primary free radicals readily become secondary radicals. The rearrangement to give tertiary radicals, as with butyl radicals, is slow.

Catalytic cracking is an ionic rather than a free radical reaction but otherwise the mechanism, involving initiation, propagation, rearrangement, and termination, is formally similar to that in Figure 4.9, except for the one termination reaction where two ions of positive charge cannot combine and an outside negative ion is required. Why then do the products differ widely? The reason is that, under cracking conditions, free radicals rearrange and fragment at roughly comparable rates, whereas carbocations rearrange much more rapidly than they fragment. Hence rearrangement to branched chain compounds is the dominant process. This relates to the relative

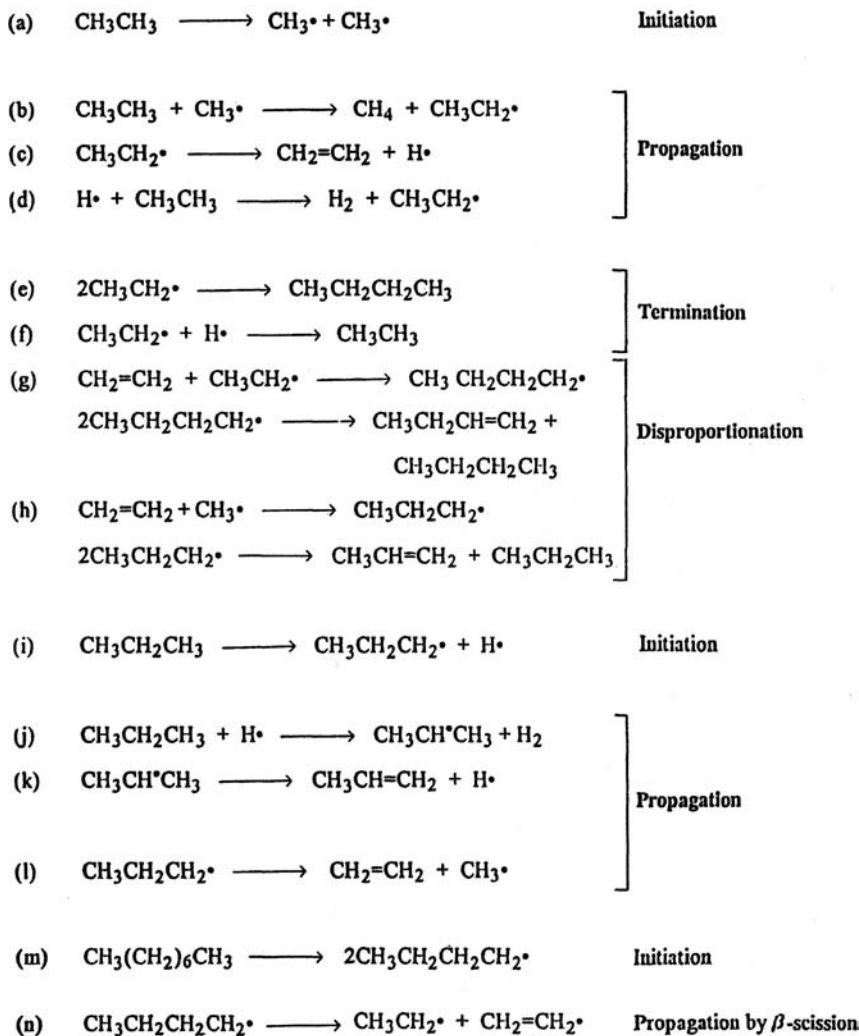


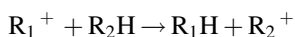
FIGURE 4.9 Mechanism of steam cracking.

stabilities of free radicals and carbocations. Tertiary free radicals are more stable than secondary radicals, which are more stable than primary. But the differences are quite small. In contrast, the differences between tertiary, secondary, and primary carbocations are very large, and such ions have a much greater tendency to rearrange. Table 4.8 indicates that the isopropyl radical is only 22 kJ/mol more stable than the *n*-propyl radical, whereas the isopropyl cation is 121 kJ/mol more stable than its *n*-propyl isomer. The differences in the case of the butyl radicals and ions are even larger. In the later stages of cracking, furthermore, fragmentation with the expulsion of a small free radical is energetically unfavorable but not markedly so, whereas expulsion

TABLE 4.8 Heats of Formation at 25°C of Radicals and Cations

$\Delta H_F^\circ(R^\cdot)$			$\Delta H_F^\circ(R^+)$	
kcal/mol	kJ/mol		kcal/mol	kJ/mol
52	217	H	364	1521
32	134	CH ₃	255	1066
25	105	C ₂ H ₅	227	949
22	92	<i>n</i> -C ₃ H ₇	222	928
17	71	<i>i</i> -C ₃ H ₇	193	807
19	79	<i>n</i> -C ₄ H ₉	218	911
13	54	<i>s</i> -C ₄ H ₉	196	819
6	25	<i>t</i> -C ₄ H ₉	171	715

of a small unstable ion is energetically highly unfavorable. Thus chain transfer to give alkanes on the lines of

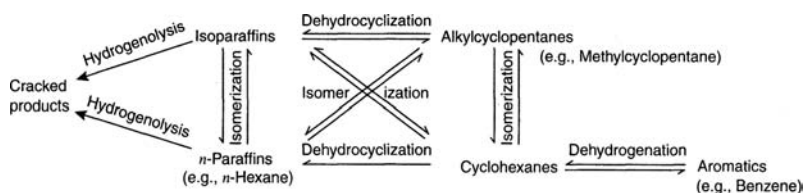


is a much more favorable reaction for small ions than fragmentation. Catalytic cracking therefore gives only alkanes with at least three carbon atoms.

4.8 CATALYTIC REFORMING

Catalytic reforming, a process first commercialized in 1950 by Universal Oil Products, converts aliphatic or cycloaliphatic compounds to aromatics. It is carried out with naphtha (Fig. 4.3), the original intention being to raise the octane number of the gasoline fraction. It has also become the major source of aromatics – benzene, toluene, and xylenes (BTX) – in the United States.

Catalytic reforming comprises three basic reactions: dehydrogenation, isomerization, and hydrogenolysis. Dehydrogenation is exemplified by the dehydrocyclization of an alkane as shown in Figure 4.10 and by the dehydrogenation of an alicyclic compound to an aromatic one. Isomerization is demonstrated by the molecular rearrangement of methylpentane to cyclohexane. Hydrogenolysis is a hydrocracking

**FIGURE 4.10** Catalytic reforming.

reaction, which takes place during catalytic reforming, in which heavy molecules are cracked into lighter ones such as propane, isobutane, and *n*-butane.

Most important are the reactions of dehydrogenation and isomerization. For these a dual function catalyst is required, in this instance platinum or rhenium supported on alumina with a chloride adjuvant that helps to achieve and maintain uniform metal dispersion. The catalyst effects two reactions. In the first, compounds are isomerized (Fig. 4.10) and in the second the isomerized products are dehydrogenated. Cyclohexane is transformed to benzene and methylcyclohexane to toluene. Thus the dual function catalyst precludes an equilibrium state by causing the product of an initial reaction (isomerization) to undergo a second reaction (aromatization) as soon as it is formed. The isomerization step is rate determining. Because it is slower than the aromatization step, there is an opportunity for the undesirable hydrogenolysis or hydrocracking reaction to occur. This can be reduced but not eliminated by lower operating pressures. The reaction is carried out at 400–500°C and 25–35 bar. Gas and hydrogen yield is about 15%, the remaining 85% comprising aromatics and unreacted feed.

The earliest catalytic reformers, in the 1950s and 1960s, did not provide for catalyst regeneration on site. Spent catalyst was replaced by fresh catalyst, and the spent catalyst was returned to the manufacture for regeneration or recovery of the platinum.

Catalyst regeneration *in situ* offers obvious advantages. The most common catalytic reforming unit today has three fixed bed reactors, and all the catalyst is regenerated during a shutdown every year or so, without its being removed from the reactors. Such units are called semiregenerative catalytic reformers (SRs).

The latest types of catalytic reformers are called continuous catalyst regeneration reformers (CCRs). Parts of the catalysts are continuously regenerated *in situ* in a special regenerator, and by continuous addition of the regenerated catalyst to the operating reactors. By 2006, two CCR versions were on offer: UOP's CCR Platformer process, and Axen's Octanizing process. The CCR process produces reformat with higher aromatics content and higher octane ratings (Table 4.9). Modern catalytic reformers are usually of this type.

TABLE 4.9 Typical Reformer Aromatic Yields

Weight Percent	SR	CCR
Hydrogen	1.7	3.0
C ₅ + reformat	81.0	83.4
LPG/gases	17.3	13.6
Reformat quality		
Benzene	5.8	9.0
Toluene	16.9	21.0
Xylenes	20.6	23.7
C ₉ aromatics	11.3	17.0
Nonaromatics	45.4	29.3
Total aromatics	54.6	70.7

Catalytic reforming provides toluene and xylenes for unleaded gasoline. These are preferred to benzene because of their higher octane number and lower toxicity. Accordingly higher molecular weight naphthas are reformed for unleaded gasoline and a surplus of light naphtha, which yields benzene, started to develop in the mid-1980s. This fraction may be isomerized to branched chain compounds, which have higher octane numbers and are less polluting than the aromatics. It may also be steam cracked to produce olefins. It cannot be reformed efficiently to benzene because yield is low owing to the facile formation of cracked products.

A typical catalytic reformate contains benzene, toluene, and xylenes in the ratios shown in Table 4.10. Toluene is the major component. The chemical industry, however, requires more benzene than toluene, so there is a mismatch. Little can be done to change the reforming yields since they depend on the composition of the feed. The problem is solved instead by hydrodealkylating toluene to benzene (Section 10.1).

The separation of the components of catalytic reformate is complicated. The gas stream from the reformer is cooled, and products containing five or more carbon atoms condense. Hydrogen and the C_1 – C_4 alkanes are taken as a top product. The hydrogen is usually used to dealkylate toluene (Section 10.1), and the alkanes are burned as fuel. The liquid product is treated with a solvent that preferentially dissolves aromatic compounds. Diethylene glycol/water, *N*-methylpyrrolidone/ethylene glycol, and sulfolane (Section 7.1.6.2) are used in various processes. Sulfolane appears to be preferred because it produces an aromatic stream with less than 1% nonaromatics. The aromatics appear in the extract, and the C_5 compounds are left in the raffinate. The solvent is distilled off and recycled, and the benzene, toluene, and mixed xylenes are separated on three fractional distillation columns, leaving a high boiling C_9 + aromatics fraction.

Separation of the mixed xylenes is difficult because their boiling points are close. The separation process is described in Chapter 11. As with benzene and toluene, the isomer distribution as shown in Table 4.11 does not match market requirements. Whereas 74% of *p*-xylene is required, nature provides about 19%. Similarly 5% of *m*-xylene is needed, whereas the C_8 fraction contains about 43%. The imbalance is corrected by isomerizing unwanted *ortho*- and *meta*-xylenes to an equilibrium mixture, which must again be separated. A zeolite catalyst, ZSM-5, is most often

TABLE 4.10 Catalytic Reformate Production Ratio Versus U.S. Chemicals Demand

	Reformate Production Ratio (%)	Chemicals Demand (%)
Benzene	11	45
Toluene	55	22.7 ^a
Xylenes	34	32.3

^a The increase in this figure since the first edition is because of a greater amount of hydrodealkylation and disproportionation.

TABLE 4.11 Equilibrium Composition of C₈ Fraction from Catalytic Reforming

Component	Weight Percent in C ₈ Fraction	Weight Percent in Pyrolysis Gasoline	End Use Requirement
Ethylbenzene	17–22	43–57	0%
<i>p</i> -Xylene	17–22	10–12	74%
<i>m</i> -Xylene	40–45	23–26	5%
<i>o</i> -Xylene	16–20	16–19	21%

used. It converts ethylbenzene to benzene, although other catalysts isomerize it to the xylene isomers.

An interesting technology developed by Chevron is in situ hydrodealkylation during catalytic reforming, the key being a zeolite catalyst such as ZSM-5 doped with platinum. The reaction is carried out at 540°C, the temperature necessary for the hydrodealkylation of both the toluene and the xylenes. Benzene and methane are the major products. The process was later modified to make benzene and toluene the major products. The zeolite decreases hydrogenolysis to lower alkanes and may even facilitate the conversion of those alkanes, once formed, to aromatics.

The mechanism of benzene formation in catalytic reforming differs from that of toluene and xylenes. The latter are obtained by dehydrogenation of alkylcyclohexanes, which in turn result from the dehydrogenation of the corresponding alkanes. Some benzene results similarly from the dehydrogenation of cyclohexane, but also catalytic reforming involves the dehydroisomerization of cyclopentanes, which combines dehydrogenation and carbenium ion reactions. A cyclopentyl cation forms, which undergoes ring opening and the subsequent formation of the cracked products shown in Figure 4.9.

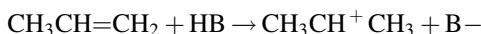
4.9 OLIGOMERIZATION

In the refinery the oligomerization of olefins is termed polymerization because the term oligomer had not been coined when the process was invented. Low molecular weight olefins produced either by steam or catalytic cracking, but usually by the latter, are dimerized and trimerized to branched chain olefins, suitable for gasoline. They may be used as such or, preferably, hydrogenated. These oligomers are called polymer gasoline or polygas. Their popularity waned with the advent of alkylation (Section 4.10), the products of which do not require hydrogenation. The removal of lead from gasoline has prompted a renewed interest in polygas.

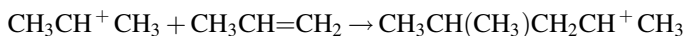
Oligomerization is carried out with propylene, 1- and 2-butenes, and isobutene traditionally with a Friedel–Crafts catalyst such as phosphoric, sulfuric, or hydrofluoric acids. More recently, solid catalysts – zeolites or acid ion exchange resins – have been introduced. In the Friedel–Crafts reaction, a low energy-content intermediate species forms readily. Because of its stability, it does not polymerize. Ethylene does not

oligomerize in this way because its intermediate species, formed only with difficulty and requiring initiators or catalysts, is highly energetic and polymerizes readily. An advantage of the oligomerization process is that dilute olefinic streams (catalytic cracker off-gases) from the refinery can be used.

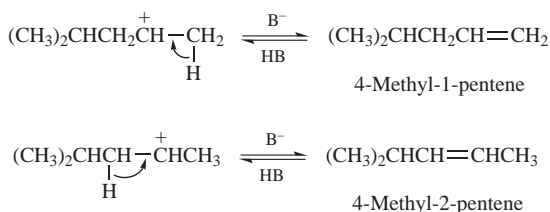
The reaction proceeds by a classical carbenium ion mechanism. In the presence of an acid catalyst (HB) the olefin takes on a proton from the catalyst to yield the carbenium ion.



This may add to another molecule of olefin in a propagation reaction to yield a new carbenium ion:

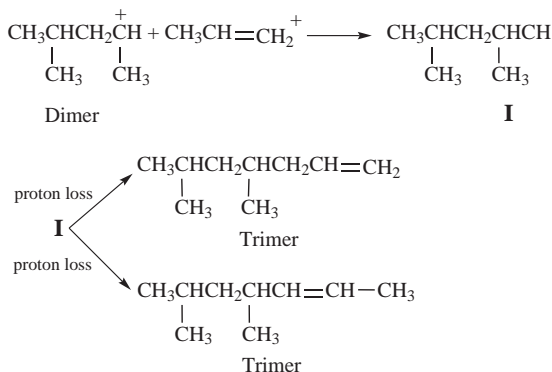


which can be stabilized or terminated by loss of a proton in one of two ways to form a dimer.

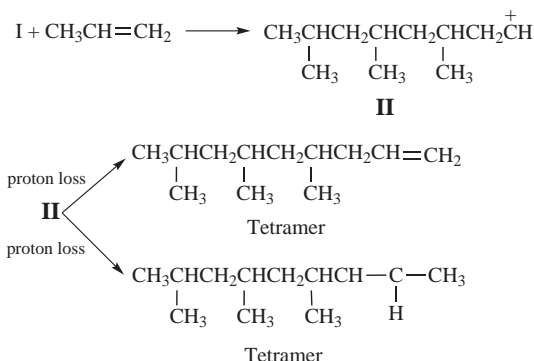


Repetition of the propagation reaction with another molecule of propylene yields isomeric trimers, and the trimeric carbenium ion may add a fourth molecule of propylene to give a mixture of tetramers. Even pentamers and hexamers may form.

Trimerization



Tetramerization

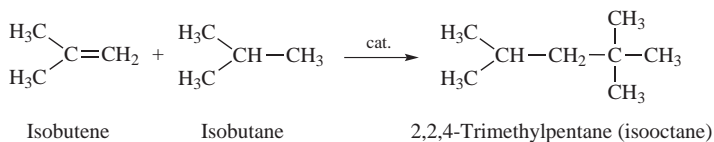


Because the intermediate species are relatively unreactive, polymers cannot be made in this way. Propylene could not be polymerized until the advent of Ziegler–Natta catalysis (Section 6.1).

The branched C_9 and C_{12} olefins have chemical uses that are discussed later (Section 6.3). Ziegler-type catalysts may be used for the oligomerization in processes such as “Dimersol” (Section 6.3).

4.10 ALKYLATION

Polymerization, involving two or three molecules of olefins, was replaced by the more sophisticated alkylation reaction between one mole each of an isoalkane and an olefin. An olefin such as isobutene is used to alkylate a branched chain hydrocarbon, usually isobutane, in the presence of Friedel–Crafts catalysts such as sulfuric acid or hydrogen fluoride:



The 2,3,4- and 2,3,3-trimethylpentanes are also formed. The interaction of propylene with isobutane yields a complex mixture including 38% 2,3-dimethylpentane and 19% 2,4-dimethylpentane. In addition, 25% propane results. The remainder is a mixture of branched chain hydrocarbons with eight carbon atoms. Since the carbenium ion intermediate attacks tertiary carbon atoms, the products are highly branched and have high octane numbers.

The octane number of a fuel is defined in terms of its knocking characteristics relative to *n*-heptane and isooctane (2,2,4-trimethylpentane), which have been arbitrarily assigned octane numbers of 0 and 100, respectively. The octane number

of an unknown fuel is the volume percent of isooctane in a blend with *n*-heptane that has the same knocking characteristics as the unknown fuel in a standard engine. Three kinds of octane numbers are recognized. The first is Research Octane Number (RON), which is the octane number measured under relatively mild test conditions. The Motor Octane Number (MON) is determined at higher engine speeds and temperature. A third octane number, Research Octane Number RON 100°C, is the RON of the fraction of the gasoline distilling below 100°C. This fraction plays a special role in controlling antiknock performance during acceleration.

The olefins for alkylation, as for oligomerization, come primarily from the off-gases from catalytic cracking. The isobutane is produced during catalytic cracking as well as in catalytic reforming. It also occurs in the gas fraction from petroleum distillation, and on-purpose isobutane is made by the isomerization of *n*-butane (Section 4.13). Hydrogen fluoride is the preferred catalyst in modern refineries because the process can operate in the liquid phase at temperatures in the range of 50°C. With sulfuric acid lower temperatures of 0–10°C are required to prevent oxidation of the olefin. Solid acid catalysts, with their nonpolluting features, are being vigorously explored. These not only solve the ecological problems associated with liquid acid catalysts but also require less capital investment, because disposal of spent catalyst is simpler, and less catalyst-handling equipment is needed.

4.11 HYDROTREATING AND COKING

Hydrotreating is a term applied to several refinery processes intended to remove impurities from petroleum and/or to reduce the viscosity of very viscous oils or “bottom of the barrel” fractions. Hydrotreating will become increasingly important when heavier more impurity-laden oils enter the refinery, as they are certain to do since the world’s reserves contain a high proportion of heavy oil. Light crude oils have a higher hydrogen-to-carbon ratio than heavy oils. Hydrotreating adds hydrogen to heavy oils so that they can be handled in a refinery like the lighter, more desirable materials. Hydrocracking is today’s best established technology for adding hydrogen to heavy fuels, particularly heavy gas oils. It can also be applied to the so-called resid fraction, the residue left when practically everything else in the petroleum barrel is removed.

Hydrocracking is a variant of hydrotreating and also of catalytic cracking. A different catalyst is used, and the cracking reactions take place in an environment of hydrogen at 60–100 bar. Because hydrogen is present the catalyst does not “coke” as it does in catalytic cracking; a wider range of feedstocks can be tolerated (e.g., heavy distillate can be used); and objectionable sulfur, nitrogen, and oxygen compounds are converted to hydrogen sulfide, ammonia, and water. The products are paraffins, not olefins, and are fairly low in aromatics and very low in sulfur. They are used for low-sulfur jet fuels and diesel fuels where lack of aromatics and absence of sulfur are desirable.

In addition to hydrocracking, there are several other forms of hydrotreating. The mildest is used to remove sulfur as hydrogen sulfide from gas oil and naphtha with a

catalyst comprising cobalt/molybdenum or nickel/molybdenum on alumina at about 300°C and 20–25 bar. Hydrotreating of vacuum gas oil (Section 4.1) is carried out for the same reason but requires a temperature of 350–400°C and a pressure of 35–55 bar. If the feed material is resid, the required temperature may be 450°C and the pressure may vary from 60 to 120 bar. Hydrotreating is also used for the refining of lubricating oils, primarily to remove waxes by cracking. This is competitive with extraction processes.

Hydrosulfurization may be considered a form of hydrotreating but is carried out under more severe conditions. The similarity is that both remove sulfur and nitrogen as H_2S and NH_3 , but hydrotreating also is intended to remove mercury and a variety of low percentage impurities. Also, hydrotreating will saturate double bonds like those in olefins, and this improves the stability of the composition. Aromatics are converted to cycloolefins and particularly to naphthas. The H_2S produced is converted to sulfur, and this is by far the largest source of sulfur in the United States.

Several newer hydrotreating processes were under development in the 1990s. One, known as Dynacracking, developed by the Hydrocarbon Research Institute, combines hydrocracking with the conversion of a portion of the feed to synthesis gas, that is, carbon monoxide and hydrogen (Section 10.4). In this way hydrogen is provided for the process. The so-called Aurabon process, developed by UOP, makes use of metals (e.g., vanadium) and sulfur present in the residual oil as catalysts. It uses less hydrogen than standard hydrocracking and removes metals efficiently, which is its principal advantage. Interest in these processes has diminished because light feedstocks have remained available, and there is less forecasted need to treat heavy oils.

Coking is the reverse of hydrotreating, for in this process the hydrogen is rejected. Thus heavy fractions are heated to produce volatiles, which are used in the refinery. The coproduct, which is impure carbon, is known as coke. If it has low sulfur and metal content, it can be used to make anodes for aluminum manufacture. Lower quality cokes can be used as fuel. Coke can also be gasified to carbon monoxide and hydrogen but seldom is (Section 10.4).

Alternate processing involves the extraction of residual oil with light solvents such as propane, butane, or pentane to remove asphalts and to provide a higher grade residual oil for hydrocracking. The asphalts can be used in paving and roofing, as fuels, and for conversion to synthesis gas.

4.12 DEHYDROGENATION

If cracking and reforming are considered dehydrogenations, then dehydrogenation is the most important reaction carried out industrially. In refinery practice, however, the term is restricted to specialized dehydrogenations such as the conversion of ethylbenzene to styrene (Section 5.9) or butenes to butadiene (Chapter 7).

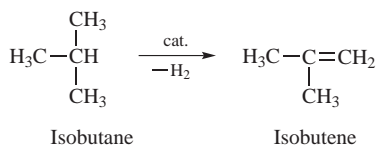
Butenes have been dehydrogenated to butadiene, particularly in the United States, where ethane and propane are steam cracked to produce primarily ethylene and propylene and lesser amounts of the C_4 olefins (Sections 4.1 and 4.15.1). Most widely used is the Houdry process. The dehydrogenation process, however, must

compete with imported butadiene and, in recent years, the latter has been more economical.

Propane dehydrogenation processes have been available for several decades but have been of little interest because of the large amount of cheap propylene produced by catalytic cracking (Section 4.8) in the United States. The possibility of a propylene shortage (Section 4.15) and improvements in catalysts have motivated their reexamination. The chemistry is simple, involving catalytic abstraction of hydrogen from propane to give propylene. The major competing reaction is cracking of propane to ethylene and methane, which, in turn, leads to hydrogenation of the ethylene to ethane. Because of thermodynamic limitations, the process is operated above 600°C in order to achieve acceptable conversions per pass, but above 700°C cracking is the dominant reaction. The major process conditions are determined by thermodynamic limitations, reaction kinetics, and economics of the conversion/selectivity relationship.

Propane dehydrogenation process technology is offered by several licensors including UOP, ABB Lummus, Linde/BASF, Snamprogetti/Yarsintez, and Krupp Uhde. The processes vary among the licensors in terms of reactor design, pressure, temperature, heating method, catalysts, and catalyst regeneration techniques. The Lummus process is a variant of the Houdry process (see above). The first propane dehydrogenation built was in Thailand. In the early 2000s there were three propane dehydrogenation plants in Asia, one in Belgium, one in Mexico, and one under construction in Spain. Several plants started up in Saudi Arabia in 2009, and new units are planned in the United States and Thailand for 2010. A large metathesis plant (Section 4.14) will account for new propylene supplies in Abu Dhabi and coal-based propylene production is scheduled to start up in China in 2010.

Dehydrogenation was used to convert isobutane to isobutene for further conversion to methyl *t*-butyl ether in the days when this chemical was booming (Section 5.2.1). The dehydrogenation goes readily because a labile tertiary hydrogen is involved.



Several companies have studied the dehydrogenation of ethane to ethylene, which goes with difficulty. The Union Carbide process makes use of an oxidative dehydrogenation at a considerably lower temperature than steam cracking (325°C versus 800°C) at a pressure of about 20 bar. A typical catalyst is a phosphorus-modified molybdenum–niobium vanadate. It is specific for the oxidative dehydrogenation of ethane, higher hydrocarbons being transformed into carbon dioxide and water. A disadvantage is that acetic acid is a major coproduct. Although this provides an effective way to make acetic acid without investment in equipment to produce synthesis gas (Section 10.4) the process must be run in such a way that the ethylene and acetic acid are produced in quantities that the market can absorb. Since over ten

times as much ethylene is used in the United States as acetic acid, there would be an embarrassing surplus of the latter, although one or two plants could be accommodated.

4.13 ISOMERIZATION

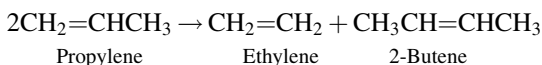
Isomerization is used to convert straight to branched chain compounds. The term may be applied to cracking and reforming reactions but usually these are excluded. In petroleum refining *n*-butane is isomerized to isobutane for alkylation to supplement isobutane from catalytic cracking and petroleum distillation. Isomerization is also used to increase the octane rating of C_5/C_6 alkanes and to convert a mixture of *m*- and *o*-xylenes and ethylbenzene from which the *p*-xylene has been extracted into a random mixture from which more *p*-xylene can be obtained.

The isomerization of C_5/C_6 alkanes for the gasoline pool is of interest. These are available since light naphtha is now used to a lesser extent in catalytic reforming because of the desire to eliminate benzene from gasoline. Although the C_5/C_6 fraction may be isomerized as such, it has been usual to remove this fraction by distillation. The *n*-pentane and *n*-hexane are isomerized to isopentane and isohexane over a fixed bed platinum catalyst in a hydrogen atmosphere, although hydrogen consumption is low.

The isomerization of *n*-butane to isobutane is effected by an aluminum chloride catalyst in either the liquid or gas phase at temperatures of around 100°C. Isobutane can readily be dehydrogenated to isobutene and the importance of this reaction has already been described (Section 4.12). The dehydrogenation is capital intensive and units are built in areas where infrastructure exists or where low cost raw materials are available, for example, U.S. Gulf Coast, Saudi Arabia, Canada, and Malaysia.

4.14 METATHESIS

Metathesis is said to be one of the most important organic chemical reactions discovered since World War II. It originated as a refinery reaction at Phillips Petroleum Company in 1964.¹⁴ This technology, the interchange of olefins, while amazing from a theoretical point of view, initially found only niche applications. The main objective was to convert cheap propylene into more valuable ethylene and butene:



The original metathesis reaction was used only in Canada by Shawinigan, the process having been instituted commercially only six and a half years after its discovery. This plant is no longer operating because of change in feedstock availability.

The reaction is reversible, however, and the potential propylene shortage (Section 6.1) has motivated a reaction with the same catalysts in which 2-butene and ethylene interchange to yield propylene.¹⁵ The shift of equilibrium to the left is achieved by recycling ethylene to give a high ethylene-to-butene ratio at the reactor inlet. In this way it is possible to obtain nearly 100% conversion of butene. The reaction can be carried out with 1-butene as well as *cis* or *trans* 2-butene provided that another catalyst is added to promote the shift of the double bond from the less thermodynamically stable 1 position to the more stable 2 position.

In 1984, Lyondell (now LyondellBasell) built a 1 billion pound per year unit to produce propylene by this reaction, which had been developed by ARCO. Thus a major use for metathesis developed, which was exactly opposite from the use that initially motivated the reaction's invention. Originally, Lyondell even made the 2-butene by dimerization of ethylene, a process pioneered by Phillips, so that the propylene product was formed entirely from ethylene. Nickel catalysts have been widely studied for this dimerization, and one described in a Phillips' patent comprises nickel oxide supported on silica and alumina. A more sophisticated catalyst later described by Phillips is tri-*n*-butylphosphine nickel dichloride mixed with ethyl aluminum dichloride. With this catalyst the reaction goes at 33°C and 12 bar to give an ethylene conversion of 93%. 2-Butene is also available from the C₄ fraction from raffinate-2 from steam or catalytic cracking (Chapter 5) and Lyondell switched to it, so that two-thirds of the propylene molecule was then derived from the cheap 2-butene.

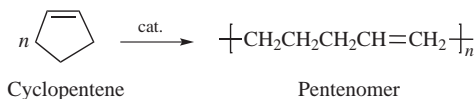
Axens (formerly IFP) has developed a similar metathesis process. However, the Axens process uses a rhenium on alumina catalyst which operates at a much lower temperature of 25–50°C in a moving bed reactor. Common to all metathesis processes is the need to remove from the feeds any polar impurities and dienes that poison the catalyst.¹⁶

In the late 1990s ABB Lummus bought the licensing rights to the Phillips metathesis technology. It has since sold over 25 licenses and, as of 2009, there were 14 units in operation. The process uses tungsten oxide on silica as the catalyst and operates at a temperature of 300–375°C in a fixed bed reactor. In 1998 BASF and Fina jointly authorized a new world scale steam cracker at Port Arthur, Texas, and have incorporated a metathesis unit to convert ethylene and butenes to propylene. The economics of the conversion vary with market prices for the feedstocks as well as the product propylene, and BASF/Fina has the flexibility to turn the unit on or off depending on market conditions. When run with it on, the new cracker has the capability of producing 860,000 metric tons/year of both ethylene and propylene per year. The residual butadiene/isobutene makes this the world's largest butadiene plant.

4.14.1 Metathesis Outside the Refinery

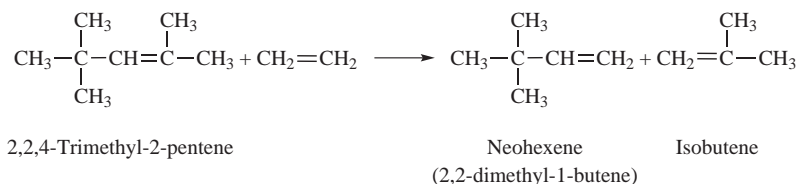
Metathesis reactions can be carried out with most olefins except those with conjugated double bonds or with functional groups near to the double bond. It has been used for the synthesis of various chemicals outside the refinery. The SHOP process is described in Section 5.3.4, but the other syntheses are described here because the original metathesis process was intended for refinery use.

When applied to cyclic compounds, metathesis yields polymers. Thus cyclopentene and cyclooctene undergo metathesis to yield specialty polymers. The one from cyclopentene is called a pentenomer.

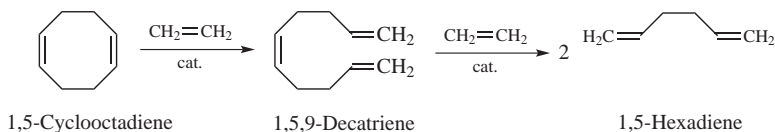


If there are nonconjugated double bonds in a cyclic structure, a crosslinked polymer forms. Hercules took advantage of this in the development of a reaction injection molding (RIM) compound comprising dicyclopentadiene and a metathesis catalyst that polymerizes it to a crosslinked structure (Section 8.2). Hercules has subsequently sold the business.

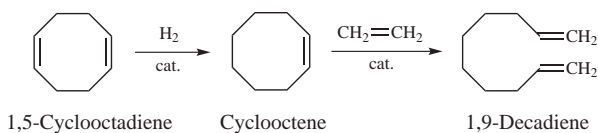
Ethylene will undergo metathesis with a mixture of diisobutene isomers. The isomer that undergoes metathesis is 2,4,4-trimethyl-2-pentene, whose internal double bond reacts most readily. A catalyst is added to isomerize other diisobutenes with terminal double bonds to the desired pentene. 2,2-Dimethyl-1-butene results together with isobutene. The branched chain product, known also as neohexene, is a precursor for the preparation of a synthetic musk fragrance.



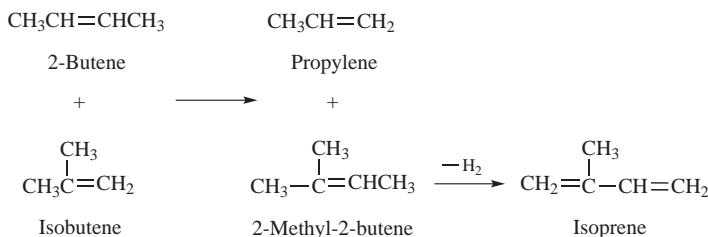
Shell has developed a metathesis route to α,ω -dienes. One such compound, 1,5-hexadiene, results from the reaction of ethylene with 1,5-cyclooctadiene, which in turn comes from the dimerization of butadiene (Section 7.1.6.2).



A related product is 1,9-decadiene made by reacting ethylene with cyclooctene, which is made by selective hydrogenation of 1,5-cyclooctadiene.



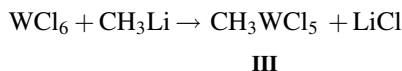
An isoprene precursor results from the metathesis of isobutene and 2-butene (Section 8.1).



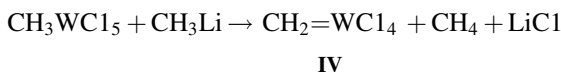
None of these three reactions was commercialized.

4.14.2 Mechanism of Metathesis

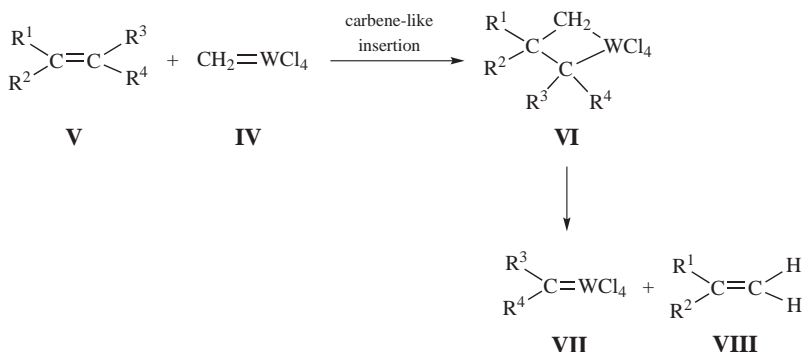
The mechanism of metathesis is intriguing because it differs from other catalytic transformations of olefins. It can best be explained if one assumes a homogeneous catalyst such as tungsten hexachloride in combination with a metal alkyl such as methyl lithium. As in all such reactions, a metal complex **III** forms first.



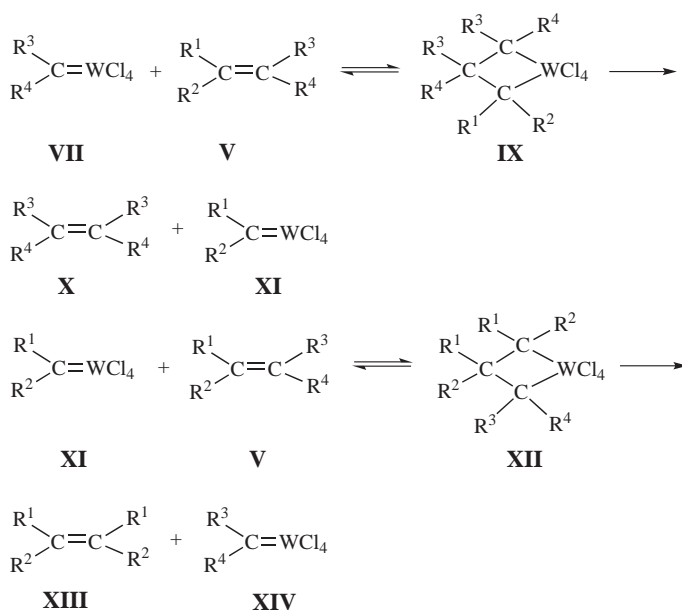
This complex reacts with more methyl lithium to form a compound with a carbon–tungsten double bond (**IV**). This is a true double bond but it may also be considered as an encumbered carbene, thus reacting like a stabilized carbene.



This catalyst brings about the rearrangement of compound (**V**), an olefin with four different R groups by the following propagation steps. The reaction of (**IV**) and (**V**) provides (**VI**), which in turn dissociates to give (**VII**) and a minor product (**VIII**).



Compound (VII), which contains alkyl groups R^3 and R^4 , reacts with more of the initial olefin to give (IX). This compound in turn dissociates to give (X) and (XI). Compound (X) is considered one of the major products of the metathesis since it contains only two of the four groups present in compound (V). The other two are resident in the catalyst complex (XI). Accordingly, (XI) reacts with the initial olefin (V) to give (XII), which can dissociate just as (IX) did to give (XIII) and (XIV). Compound (XIII), the counterpart of (VIII), contains the other two groups present in the initial olefin (V). The catalyst complex (XIV) can then continue the reaction just as the complex (XI) did.



The dissociation reactions are mechanistically the inverse of the carbene-like insertion reactions. These reactions are also reversible, but such reversions have no observable consequences. Termination steps are obscure and presumably are brought about by impurities and possibly by dimerization of the catalyst.

The conventional cross-metathesis process, in which two alkene give a much longer chain and a much shorter chain alkene, gives the only most energetically stable isomer. This is called the *E* isomer, and the two chemical groups on either side of the double bond are as far away from each other as possible. A recent development gives the less stable *Z* isomer, with the aid of catalytic molybdenum complex. It gives *Z* alkenes from enol ethers and allylic amides and has been used to synthesize a phospholipid implicated in Alzheimer's disease and a potent immunostimulant KR7000.¹⁷ Other undisclosed industrial applications are said to be taking place.

4.15 FUNCTION OF THE REFINERY AND THE POTENTIAL PETROLEUM SHORTAGE

A major objective of the U.S. refinery has traditionally been to produce high octane gasoline. To be sure, the fractions heavier than naphtha (Fig. 4.2) were important for aviation, diesel, boiler and heating fuels, lubricants, and paving materials, but production was driven by the demand for gasoline. Because of need for high octane number, catalytic cracking was developed and always played a far more important role in American refineries than it did in refineries in Europe and Japan that were geared to production of fuel oil, since much less gasoline was needed and cheap coal was not available.

The refinery reactions (Sections 4.8, 4.9, and 4.10) of oligomerization, alkylation, and catalytic reforming were all devised to raise octane number as were lead tetraalkyls. The many catalytic crackers in the United States produced large quantities of C_3 and C_4 olefins, and it was these that provided feed for the oligomerization and alkylation reactions. They also proved useful in chemical reactions for cumene (Section 6.6) and isopropanol production (Section 6.7).

Catalytic crackers give C_3 and C_4 olefins in more dilute form than do steam crackers (Section 4.6). The dilute streams, which contain propane, are less economic for use by the chemical industry except for production of cumene and isopropanol. In any case the refinery had first call on the olefins for polymer gasoline (Section 4.9) and alkylation (Section 4.10) and also for adding to LPG. The remainder could be upgraded for the chemical industry, despite the higher cost. The supply is still large because of the many catalytic crackers. In 2008 the refinery provided 38% of the chemical industry's propylene in the United States, down from 52% in 2002.

In Europe, the situation is reversed. Less refinery propylene is produced in catalytic crackers (because there are fewer of them) and more is produced from steam cracking (because much more naphtha is cracked). Catalytic cracking in 2008 provided about 28% of the European chemical industry's 14.8 million metric tons of propylene, up from 20% in 2001, so the transatlantic patterns are drawing closer together. Because of Europe's longstanding propylene shortage, an effort was made to obtain more propylene from the refinery, but this was only moderately successful. The deficit in supply was made up by imports in 2002, which amounted to about 0.33 million metric tons, but this had changed to a positive trade balance of 0.13 million metric tons by 2009.

The rise in gasoline prices in the 1970s led to the disappearance of the great American gas guzzler and the production of smaller, lighter cars with lower gasoline consumption. Also, diesel fuel became popular. With lower gasoline production, there was lower production of the middle distillate (gas oil fraction, Fig. 4.2) from which diesel fuel comes. Thus the cost of diesel fuel also increased and, in Europe, Japan and Southeast Asia, there were threatened shortages.

Shell was motivated to develop a process based on Fischer-Tropsch technology to make diesel fuel, lubricants, and wax for candles (Section 14.2) and built a plant in Malaysia.

4.15.1 Unleaded Gasoline and the Clean Air Act

The advent of unleaded gasoline provided a “dislocation,” but the refineries in the United States accommodated to it well. Some oligomerization units (Section 4.9) were reactivated to obtain branched chain, high octane number olefins. These had been shut down in the 1960s in favor of alkylation (Section 4.10), which unleaded gasoline caused to become much more important. Catalytic cracking catalysts were improved so that higher octane products resulted. Refiners raised the octane number of gasoline by including higher amounts of aromatics such as toluene and xylenes made by catalytic reforming (Section 4.8).¹⁸

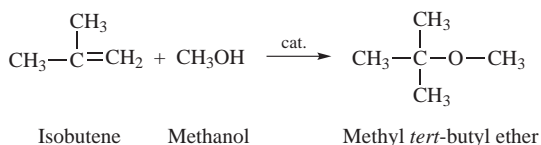
In 1991 a much greater dislocation was provided by the Clean Air Act. It became necessary to reduce benzene content of gasoline from about 3% to 1%. In nine areas in the United States, where pollution exceeded levels specified by the Environmental Protection Agency, aromatics (i.e., toluene and xylenes) content had to be reduced from 36% to 25% by 1995. Ironically, this occurred after some refineries had increased their capacity for manufacturing aromatics, to maintain octane number.

There were at least three scenarios for achieving the 1% benzene level. Refineries in the early 1990s stripped naphtha to remove the low-boiling C₅–C₆ fraction, to minimize benzene formation in catalytic reforming. The fraction in turn became available for isomerization to branched chain, higher octane number components (Section 4.13) and for cracking to olefins. Carried to the extreme, a benzene shortage for the chemical industry might have resulted. Even so some benzene always forms in catalytic reforming, because of hydrodealkylation (Section 10.1) of toluene and xylenes.

A second possibility was to remove the benzene by distillation. This would have added about 150,000 metric tons of benzene to the current U.S. supply, which would not have been disruptive. On the other hand, the decision to extract benzene from gasoline in Western Europe would have increased supply by 450,000 metric tons. The fact that Western Europe still imports benzene (Fig. 2.10) indicates that this course was not chosen.

A third scenario was for the refinery to produce two reformates, one with as little benzene as possible for gasoline, and the other containing benzene for the chemical industry. This was disruptive for the refinery, which is programmed to carry out continuous reactions without interruption. Nonetheless, this was the approach adopted.

The next problem was how to compensate for the octane number lost by removal of lead compounds and the drastic reduction of aromatics content. The answer was found in oxygenates, compounds that are primarily the province of the chemical industry, and the Clean Air Act specified that the reformulated gasoline had to contain compounds that contributed 2.7% oxygen. The best oxygenate at the time appeared to be methyl *tert*-butyl ether (MTBE) made by reacting isobutene with methanol over an acid catalyst, usually an acidic ion exchange resin.



To contribute this amount of oxygen, MTBE content must be about 17%.

The sources of isobutene at the time were raffinate-1 from the refinery, off-gases from catalytic cracking, and as a by-product from propylene oxide production, where it came from the facile dehydration of the *tert*-butanol coproduct (Section 6.8). There was not enough isobutene in the world from these sources to make the amount of MTBE required, and a further process for its production from *n*-butane was developed (Section 4.13). It suddenly became an important chemical, whereas in the past it had always been a cheap by-product.

From 1995 the United States imported about 4 million metric tons/year of MTBE and probably one-half the methanol needed to make MTBE domestically. By 2000, the market had risen to 13.5 million metric tons (Section 1.3.6) and production to 9.1 million metric tons. West European production was about 3 million metric tons and world production in 1998 was 18.2 million metric tons. The isobutene for U.S. MTBE production came mainly from *n*-butane via isobutane (53.9%) with smaller amounts from *tert*-butanol dehydration (24.3%), catalytic cracking (12.4%), and steam cracking (9.3%).

It was then realized that MTBE was contaminating groundwater. The point is that most gas stations store their gasoline in underground tanks and, over the years, these deteriorate. Strict regulations exist in the United States and Europe to prevent this, but they are inadequately enforced. Slight damage to tanks is unimportant, because gasoline is hydrophobic and therefore does not leak readily into damp subsoil nor diffuse through it rapidly. MTBE, however, is sparingly soluble (4.8 g per 100 g water) and both leaks and diffuses. Even in tiny concentrations, it has a strong terpene-like odor and gives a bitter taste to water, even though it is not highly toxic. Like many branched chain materials, it biodegrades slowly. California arbitrarily decided to phase out MTBE by 2002 and 24 other states had followed suit by 2005. The requirement for 2% oxygenate requirement in reformulated gasoline was repealed. Although not all states had legislated, oil companies discontinued the use of MTBE throughout the United States.¹⁹

To maintain the octane number of gasoline and conform to the clean air legislation, ethanol was introduced into reformulated gasoline blends to replace MTBE. Its high volatility was a drawback. Nevertheless, for complicated reasons – environmental considerations plus political pressure from corn growers – subsidized fermentation ethanol has become the oxygenate of choice. As its addition to the 10% level is mandatory in some U.S. states and cities, there is the incongruous situation of the government subsidizing a mandated product.

Ethanol is also used as a motor fuel as such and in combination with hydrocarbon fuels in Brazil. Brazilian alcohol, however, is made by the fermentation of juice from sugar cane, which has a much higher carbohydrate content than does corn, which yields the starch used as a raw material in the United States. Also, the sugar cane juice is obtained simply by crushing the cane and is thus cheap, whereas starch isolation is a relatively expensive and energy-intensive process. Even in Brazil, however, its use is not economic, even though the energy for distilling the alcohol comes partly from burning bagasse, the sugar cane residue.

The use of fermentation alcohol represents a trend toward renewable raw materials for commodity chemicals. All the same, it is difficult to think of ethanol as a renewable resource unless it generates more energy as a motor fuel than is spent in its production and purification (Section 16.6.5) and this is an area of debate. The deficit, if it exists, comes from petroleum and natural gas. The possibility of retrofitting methanol plants so that they will produce mixtures of higher alcohols has also been studied but does not appear economic. Ethyl *t*-butyl ether (ETBE) is acceptable in unleaded gasoline and results from the interaction of ethanol and isobutene. It is less soluble than MTBE and is less volatile than ethanol. It is mainly used in Europe.

Methanol has been studied as a neat automotive fuel and as a component in petroleum-based gasoline. Because it separates out in the presence of a small amount of moisture, gasoline containing it must include a cosolvent alcohol. *t*-Butanol has been used with methanol in a proprietary product known as "Oxinol." It is not, however, as effective as MTBE. Methanol is of particular interest for replacing diesel fuel in trucks and buses. It is available cheaply from many parts of the world where natural gas is in surplus, and huge excesses were in prospect in the early 2000s because of the construction of giant plants. The banning of MTBE has freed further large tonnages.

The final alcohol that has been used in gasoline is isopropanol, which is also an acceptable oxygenate and can be made from refinery propylene. It was marketed in the United Kingdom after World War II under the name "Cleveland Discol."

Still another part of the dislocation due to the Clean Air Act was the decreased supply of hydrogen that occurred in the already hydrogen-deficient refinery when catalytic reforming was drastically reduced, because aromatics content was decreased. On-purpose hydrogen had to be manufactured.

4.16 SEPARATION OF NATURAL GAS

Natural gas is almost entirely methane, but most American natural gases contain recoverable amounts of ethane, propane, butane, and higher alkanes. Similar mixtures are obtained from the "associated gas" from oil wells. These may be extracted as feedstock for steam crackers. At the wellhead, the gas is at a high pressure (30–100 bar), and propane and higher alkanes may be absorbed in a high boiling oil at ambient temperature and subsequently purified by low temperature fractional distillation. Ethane may be absorbed similarly at -50°C . Hydrogen sulfide and carbon dioxide are scrubbed out with aqueous mono- or diethanolamine (Section 5.11.6.4), and water removed with hygroscopic diethylene glycol (Section 5.11.6.2). Even when most C_2+ compounds are removed, some ethane is usually retained in natural gas to raise its BTU content to the value demanded for heating gas.

Thus natural gas provides the chemical industry with methane primarily for conversion to synthesis gas (Section 12.5), ethane and propane for steam cracking to olefins, and butane, which is oxidized to maleic anhydride (Section 7.4.2) and isomerized to isobutane (Section 4.13).

4.17 OIL FROM TAR SANDS

The technology of drilling for oil in conventional oil fields is well documented elsewhere, but it is appropriate to describe briefly here two methods of extracting oil from Canadian tar sands.²⁰ About 97% of Canadian oil reserves lie in tar sands, which are a mixture of sand, water, clay, and bitumen in northern Alberta and Saskatchewan. The technology depends on the depth at which the tar is buried. If it is 60 m (200 ft) below the surface, the topsoil is bulldozed away and stored for reclamation. Mining shovels dig up the sand and load it into trucks. This is not as easy as it sounds. In summer, the sands are warm and fluid, and the mining vehicles are liable to sink into them. In the winter, they are frozen solid and are abrasive and difficult to shovel. Once excavated, the sand is put through a crusher; hot water is added and the resulting mixture piped to an extraction plant.

If the tar sands are deeper than 60 m, wells are drilled and high-pressure steam injected into the tar layer. The steam diffuses into the tar sands and heats them. The water separates the bitumen from the sand, while the heat softens it and allows it to flow to the wells, whence it is pumped to the surface.

The bitumen resembles the heavy oil fractions retained by petroleum distillation. It is subjected to hydrodemetallization, hydrosulfurization, and hydrodenitrogenization before it can be catalytically hydrocracked to give useful products (Section 4.11).²¹

The extraction of oil from tar sands is fraught with environmental problems. It is said to destroy boreal or northern forests and to generate two to four times the amount of greenhouse gases as drilling for conventional oil. It uses 2–4.5 liters of water for every liter of oil. A proposed pipeline from Hardisty, Alberta, to Port Arthur, Texas, carries additional threats of spills and interference with the caribou.

Meanwhile, the tar sands provide almost inexhaustible reserves of oil. More crude oil and petroleum products are shipped to the United States from Canada than from any other country. In 2009 Canada shipped 1,943,000 barrels of oil per day and 536,000 barrels of petroleum products, compared with 980,000 barrels of oil products from Saudi Arabia and 24,000 barrels of petroleum products. Furthermore, Canada is close, friendly, and democratic. If the United States does not take the tar sands, China will. Between August 2009 and January 2011, Chinese companies spent \$13 billion on six Canadian tar sands and shale gas projects.²² The caribou are right to be worried.

ENDNOTES

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8. M. Burke, *Chem. Ind.*, 11 April 2011, pp. 25–27; *TIME* magazine, 31 March 2011; and many articles elsewhere.
9. *Discovery* magazine, <http://news.discovery.com/earth/hydrofracking-shale-methane-leak-in-wells-110511.html>.
10. *CHEMTECH*, 2 March 1976, p. 180.
11. Ethylene production technologies and cost of production economics are discussed in Nexant ChemSystems PERP report 00/01-4, *Ethylene/Propylene* (June 2001).
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18. An early article on the effect of unleaded gasoline on the chemical industry is H. Wittcoff, *J. Chem. Ed.*, **64**, 773, 1987.
19. http://www.chemsystems.com/about/cs/news/items/PERP0607S12_MTBE.cfm.
20. For more detail see http://en.wikipedia.org/wiki/Oil_sands.
21. Use of hydrocracking on residues from petroleum distillation as well as coal-derived liquids, shale oil, and tar sands is described in an article in *Chem. Week*, 18 February 1976, p. 69.
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CHAPTER 5

Chemicals and Polymers from Ethylene

We have described how the petroleum refinery, the steam crackers, and the catalytic reformers provide six of the seven raw materials on which the petrochemical industry is based. The seventh, methane, comes from natural gas. We can now examine the extensive chemistry associated with each of these building blocks. We start with ethylene not only because it has the simplest structure but also because it is the most important in terms of tonnage.

In 2009 the world consumed about 114 million metric tons of ethylene. This in turn (Section 1.5) was converted to about 500 million metric tons of chemicals and polymers, a figure that includes the intermediate products and the ethylene itself. By 2020 it is forecast that global production will be 174 million metric tons. To illustrate the importance of ethylene to the petrochemical industry, global ethylene, propylene, and benzene production data over a 20 year period are shown in Figure 5.1.

About 80% of all the ethylene produced is destined to end up as thermoplastic polymers or oligomers. Ethylene is itself a monomer for low, high, and linear low density polyethylenes as well as for ethylene oligomers. It is the raw material for other important monomers including vinyl chloride, vinyl acetate, styrene, and ethylene glycol. Some of these monomers also have nonpolymer uses. Thus ethylene glycol is the main component of antifreeze and ethanol, another ethylene based chemical, is a versatile solvent.

The major chemicals and polymers from ethylene are shown in Figure 5.2. The figure is deceptively simple since many of the reactions are multistep and the intermediates have uses in their own right. Even so, the chart demonstrates a basic tenet of industrial organic chemistry, namely, that most of the tonnage of the industry derives from relatively few materials. The major chemistry of ethylene can be divided into three categories: polymerization and oligomerization; four oxidation reactions

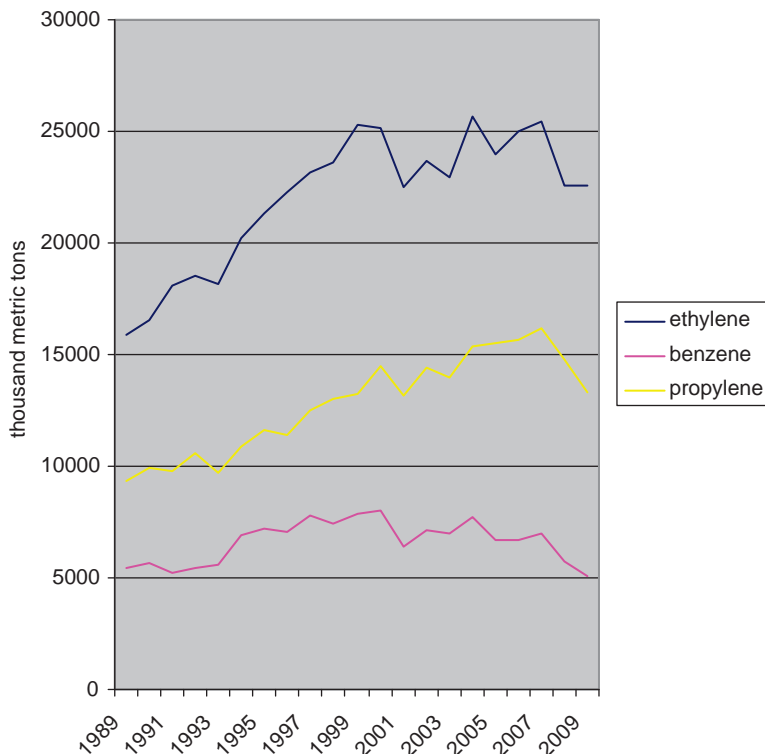
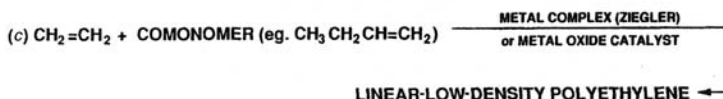


FIGURE 5.1 United States ethylene, propylene, and benzene production, 1989–2009.

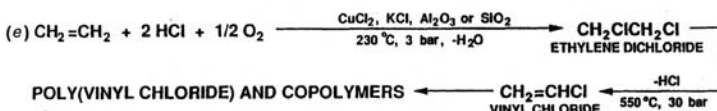
practically unknown in textbook organic chemistry; and two reactions termed “classical” because they are typical of textbook chemistry. Some of the smaller volume chemicals and polymers from ethylene are listed in Table 5.1 with references to where they are discussed. Figure 5.3 shows the end-use breakdown in the United States, Western Europe, and Asia-Pacific. All three areas devote about the same proportion of ethylene consumption to polyethylenes, but West Europeans use more LDPE and less LLDPE and HDPE than the other areas. It goes mainly into film. Asia-Pacific uses a higher proportion of ethylene oxide, probably as a feedstock for ethylene glycol and polyester fibers. Western Europe still makes petrochemical ethanol (0.8%) and acetaldehyde (0.6%).

The price of ethylene has fluctuated with the price of feedstocks and the cyclical nature of the chemical industry, but it is significant that it is still in the same price range in constant dollars that it was thirty years ago. Note that the price of any commodity is set by the costs of the least efficient producer who has stayed in business. Very cheap ethylene from the Middle East is not sufficient to supply the world market; hence the price is set by the marginal producer, in this case one based on naphtha.

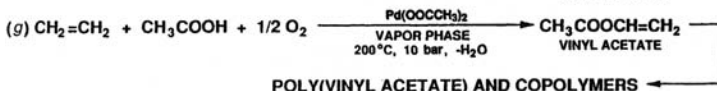
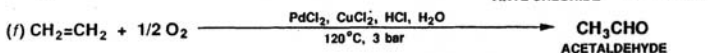
POLYMERIZATION AND OLIGOMERIZATION



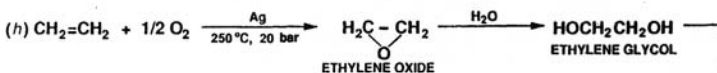
OXIDATION REACTIONS



POLY(VINYL CHLORIDE) AND COPOLYMERS

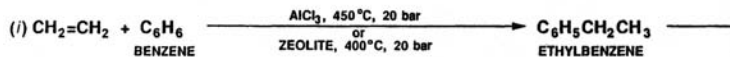


POLY(VINYL ACETATE) AND COPOLYMERS



SATURATED POLYESTER (WITH TEREPHTHALIC ACID)

"CLASSICAL REACTIONS"



POLYSTYRENE AND COPOLYMERS

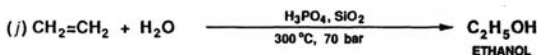
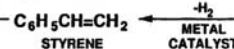


FIGURE 5.2 Major chemicals and polymers from ethylene.

5.1 ETHYLENE POLYMERS

Polyethylene is the world's largest volume polymer. Global polyethylene consumption in 2009 was about 67 million metric tons, 45% of which was accounted for by

TABLE 5.1 Some Lesser Volume Chemicals and Polymers from Ethylene

Polymers ^a	Chemicals ^a	
Very high molecular weight polyethylene (5.1.5)	Propionaldehyde (5.11.1)	Trichloroethylene (5.11.7)
Very low density polyethylene (5.1.7)	Propionic acid (5.11.1)	Perchloroethylene (5.11.7)
Chlorosulfonated polyethylene (5.2.1)	<i>n</i> -Propanol (5.11.1)	Ethylene glycol oligomers (5.11.6.1)
Ethylene–vinyl acetate (5.2.2)	Ethyl chloride (5.11.2)	Glycol ethers and esters (5.11.6.2)
Ethylene–vinyl alcohol (5.2.2)	Ethyl bromide (5.11.2)	Ethylene carbonate (5.11.6.3)
Ethylene–ethyl acrylate (5.2.2)	Chemicals from acetaldehyde (5.11.3)	Aminoethyl alcohols (5.11.6.4)
Ethylene–methyl methacrylate (5.2.2)	Metal complexes (5.11.4)	1,3-Propanediol (5.11.6.6)
Ethylene–butyl acrylate (5.2.2)	Ethylene diamine and related compounds (5.11.5)	Vinyl fluoride (5.11.8)
Ethylene–acrylic acid ionomer (5.2.3)	Ethylamines (5.11.10)	Vinylidene fluoride (5.11.8)
Polyethylene–nylon blends (5.2.4)	Ethyleneimine (5.11.6.5)	Ethylene dibromide (5.11.9)
Ethylene–propylene elastomers (5.2.5)	Vinylidene chloride (5.11.7)	Vinyl esters and ethers (5.11.11)

^aNumbers in parentheses show the sections where the chemicals are discussed.

high density polyethylene (HDPE) and the remaining 55% by low density and linear low density polyethylenes (LDPE and LLDPE). These are the three important forms of polyethylene.

5.1.1 Discovery of Low and High Density Polyethylenes

The discovery of low density polyethylene in 1932 was serendipitous. Fawcett and Gibson at ICI in Runcorn, England, were studying chemical reactions at high pressures, hoping to make synthetic rubber from ethylene and benzaldehyde. They were also interested in synthetic gasoline. ICI was studying high temperature chemistry to catch up with the German IG Farben. DuPont decided to investigate polymers for similar reasons. ICI discovered LDPE and DuPont discovered nylon. ICI's discovery hinged on a leaking autoclave. It had been pumped up to reaction pressure and allowed to stand over the weekend prior to Fawcett and Gibson performing the reaction. Pressure was lost during this period because of an ethylene leak, and more ethylene was added to the reactor which, at this stage, contained traces of oxygen from the air that replaced the leaking ethylene. The pressure of the autoclave was raised to 2000 bar and the temperature increased to 200°C. Subsequently, when cooled to room temperature, the reactor turned out to be coated with a

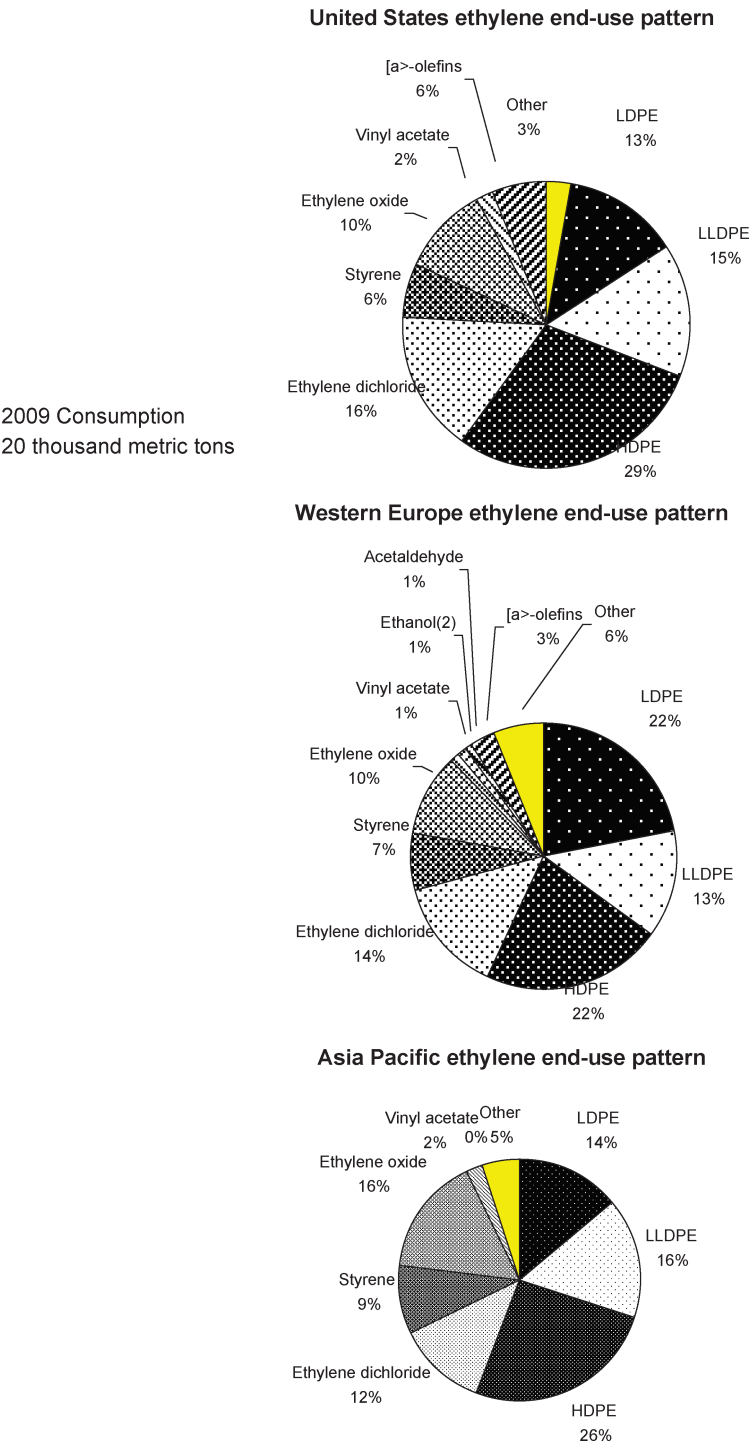


FIGURE 5.3 Ethylene end-use patterns.

white powder resembling paraffin wax, and the benzaldehyde was intact. After many more experiments, it was realized that oxygen was serving as an initiator for the polymerization of the ethylene.

The conventional wisdom of the 1930s dictated that polyethylene could not be made, because it was impossible to put sufficient energy into the ethylene molecule to achieve the transition state. It was quite possible, however, at high pressures and in the presence of a free radical initiator such as oxygen or various peroxides. The high pressures favor the polymerization reaction thermodynamically.

The discovery of high density polyethylene was similarly serendipitous. Investigators at Standard Oil of Indiana and Phillips Petroleum were seeking to oligomerize ethylene to gasoline-size molecules. They were surprised to obtain instead a stiff form of polyethylene. Whereas low density polyethylene finds its greatest use in the manufacture of film, the stiffer linear high-density material enjoys its major applications in the manufacture of bottles by blow molding and in structural parts by injection molding.

The first linear polyethylene was probably made in 1950 at Standard Oil of Indiana by Zletz, who observed that a molybdenum oxide catalyst on silica at mild temperatures and pressures did not give oligomers but rather high density polyethylene. Soon thereafter, Banks and Hogan at Phillips Petroleum obtained similar results with a catalyst comprising chromium oxide supported on silica or alumina. Phillips developed and licensed its process aggressively. Hula hoops amazingly provided the first application for the new product.

In 1954, Karl Ziegler announced his discovery. He was successfully studying ethylene oligomerization reactions (Section 5.3.2) based on aluminum alkyls. A metal salt impurity in the reaction mixture led serendipitously to the formation of high molecular weight linear polyethylene. From this evolved the famous Ziegler catalyst, typical of which is a combination of aluminum triethyl with titanium tetrachloride. The Ziegler process attracted great theoretical as well as practical interest because it can be applied to propylene (Section 6.1.1) and to practically any unsaturated compound. In contrast, the metal oxide processes are effective, for practical purposes, only with ethylene. Investigators at Standard Oil of Indiana and Phillips Petroleum tried to make polypropylene with their catalysts but obtained insignificant yields. But these experiments were carefully recorded and made Phillips the victor in a patent lawsuit with many contenders. The Ziegler process accounts for 60% of the HDPE produced in both the United States and Western Europe. A relatively recent development is the use of metallocenes or single site catalysts. These are described in Section 17.3.12.

5.1.2 Low Density Polyethylene

LDPE may be manufactured batchwise in an autoclave or, more commonly, in a tubular reactor, which makes possible continuous processing and easier heat removal. Batch-produced product is useful for paper or cardboard extrusion coating, where its highly branched structure is advantageous. The somewhat less branched continuously produced product is useful for film. About 35% of the ethylene is allowed to react in

TABLE 5.2 Properties of Polyethylenes

	LDPE	HDPE	LLDPE
Initiator or catalyst	Oxygen or organic peroxide	Ziegler or Phillips catalyst	Ziegler or Phillips catalyst
Reaction temperature	200–300°C	As low as 60°C	As low as 60°C
Pressure (bar)	1300–2600	1–300	1–300
Structure	Branched	Linear	Linear with short branches
Approximate crystallinity	55%	85–95%	55%
Comonomer	None	1-Butene ^a	1-Butene, 1-hexene, or 1-octene
Tensile strength (psi)	1200–2000	3000–5500	2000–2500
(tonnes/m ²)	850–1400	2100–3900	1400–1800
Elongation at break (%)	500	10–1000	500
Density (g/cm ³)	0.915–0.925	0.945–0.965	0.915–0.925

^a One percent as compared with 6–8% for LLDPE.

the continuous process, and the remaining 65% is recycled. This is termed 35% conversion per pass and is necessary to eliminate excess branching. With high density polyethylene, branching is not a problem, and conversion may be 100%. The properties of low and high density polyethylenes are listed in Table 5.2.

The branched structure of low density polyethylene profoundly affects its properties. Because of steric hindrance from the branching, the polymer chains cannot get as close together as they can in HDPE. Hence the crystallinity is on the order of 55% as compared to 85–95% for HDPE. The crystalline melting point, softening point, and tensile strength of LDPE are all a function of the branched structure and are considerably lower than the corresponding values for HDPE. On the other hand, the softer LDPE shows higher elongation at break and higher impact strength than does the rigid HDPE. It is also translucent rather than opaque because of its lower crystallinity. Opacity occurs because the amorphous and crystalline portions of the polymer transmit light at different rates; that is, they have different refractive indexes. Light is scattered at the crystal boundaries because of the change in refractive index (Section 17.5.1). The difference in densities, which characterizes the two polymers, is on the order of 0.3–0.4 g/cm³. The density of LDPE may be as low as 0.915 g/cm³ and of HDPE as high as 0.965 g/cm³.

The advent of linear low density polyethylene (Section 5.1.4) produced by low pressure processes was expected to make LDPE obsolete. The development of traditional high pressure technology virtually stopped. There was similarly a hiatus in the building of new high pressure LDPE plants, and some older units were closed. In practice, the new LLDPE was disappointing in some key performance areas, most notably processability (bubble stability) and optical properties (clarity, haze, and gloss). Thus the demand for LDPE continued, particularly in Europe. The underinvestment in new high pressure capacity led to high utilization rates, and markets became tight. Thus LDPE commanded a premium price over LLDPE. The growing

realization that LLDPE properties were unlikely to be engineered to match those of LDPE even in the medium term, plus the good financial performance of LDPE facilities, have renewed interest in LDPE.

Increased plant size leads to reduced investment per metric ton of capacity, improving production economics to the point that LDPE can compete with LLDPE. The higher capital and energy requirements of LDPE compared to LLDPE are offset by reduced costs of catalyst and comonomers, and the higher price achieved by LDPE coupled with typically lower license fees can make investment economics attractive. These developments have been confined to tubular reactors, with little development in the autoclave process. The combination of the rationalization of capacity (mostly autoclave) and the larger sized tubular reactors has led to the reversal of relative market share between the processes, and in 2008 tubular reactors composed about 60% of the world's LDPE capacity with autoclave reactors sharing about 40%.¹

5.1.3 High Density Polyethylene

Most HDPE is actually a copolymer containing very small amounts of 1-butene, 1-hexene, or 1-octene. The comonomer is required, particularly when metal oxide catalysts are used, to avoid formation of molecular weights so high that the polymer becomes intractable. The copolymer also has improved low temperature properties.

The production of HDPE is much less energy intensive than is that of LDPE. Reaction temperatures can be as low as 60°C and pressures as low as 1 atmosphere. Nonetheless, temperatures of 130–270°C and pressures of 10–160 bar are used commercially. Conversion per pass approaches 100%.

High density polyethylene is manufactured in solution, slurry, or fluidized bed gas phase processes. In the slurry process, the catalyst is dispersed in a solvent such as hexane, and the ethylene is polymerized batchwise in a series of reactors. The reactors can be either stirred tanks or pipe reactors in the form of a loop. Slurry processes make up about 70% of global HDPE capacity. The gas phase, fluidized bed processes were devised first by Union Carbide (now owned by Dow Chemical) and subsequently by BP and BASF. Small HDPE particles are fluidized by gaseous ethylene and comonomer (e.g., 1-butene) at 85–105°C and 20 bar. Catalyst is continuously sprayed into the reactor. The ethylene and comonomer copolymerize around the preformed polymer particles. At the same time, the gaseous ethylene removes the heat of reaction.

The initial particles grow to an average diameter of 500 microns over a period of 3–5 hours, during which time only about 2–3% of the ethylene polymerizes. The unconverted reactants are recycled. Polyethylene, once prepared, is melted, mixed with stabilizers and other additives, and extruded to form spaghetti-like rods, which are then cut into small pellets. The extrusion is an energy-intensive operation. An objective of the Unipol fluidized bed process, not achieved initially, was to obtain the polymer as a powder with uniform sized particles that could be used as such for molding and extrusion. Further development has apparently made this possible, although the value of the powder is questionable, because its low bulk density

increases shipping costs. But, serendipitously, the gas phase process has proved to be an economical way to prepare both high and linear low density polyethylenes. Gas phase processes compose about 25% of total HDPE capacity.

5.1.4 Linear Low Density Polyethylene

Linear low density polyethylene (LLDPE) is the successful result of a desire to prepare low density polyethylene by the less energy-intensive conditions used for high density polyethylene. High density polyethylene copolymers with relatively high comonomer content have been known for many years. Their density was less than that of HDPE, their crystallinity was lower, and the properties that depended on crystallinity were altered. Considerable time elapsed before it was recognized that a copolymer of HDPE, in which crystallinity had been reduced to about 55% (the crystallinity of LDPE, see Table 5.1) and its density to about 0.925, had many of the characteristics of low density polyethylene. Thus a copolymer of ethylene and 6–8 weight percent 1-butene – several times as much comonomer as is used for HDPE – resembles LDPE. 1-Hexene and 1-octene are also used as comonomers. Dow is said to use 2–4% of the latter. Like the other polyethylenes, LDPE may be manufactured by solution, slurry, or fluidized bed processes. However, gas phase processes, especially Dow's Unipol, dominate the LLDPE business. Advantages claimed for gas phase processes include simple process designs that are scaleable to very large single line capacities, and the ability to offer a wide product range with respect to comonomer, density, melt flow index (MFI), and catalyst type (Ziegler and metallocene).

The serendipity leading to several of the polyethylenes, and the fact that copolymers of the above type were known before they were recognized as economically useful, emphasizes the importance not only of discovery but of its recognition. As Louis Pasteur remarked, "where observation is concerned, chance favors only the prepared mind."

LLDPE, like LDPE, has branching that inhibits close approach of polymer molecules to one another and decreases crystallinity. The branching in LDPE is irregular and, if the LDPE is prepared by the autoclave process, there are secondary branches on the primary ones. LLDPE has regular branching because of the pendant C_2 groups provided by the 1-butene comonomer. This uniformity makes possible closer association of the polymer molecules in the crystalline portion for which reason LLDPE has a higher tensile strength than LDPE, allowing the use of thinner or lower gauge films.

Its growth in the United States was rapid at first and almost completely at the expense of LDPE. Growth was facilitated because LLDPE could be processed in HDPE equipment. Subsequently, new uses for it were found in stretch wrap film, injection molding, and rotomolding, applications for which LDPE is not suitable. The cost advantage provided for LLDPE manufacture by lower energy use is in large part counterbalanced by the cost of the more expensive monomer, 1-butene, which became one of the fastest growing chemicals of the mid-1980s. Newer processes for LLDPE make use of 1-hexene, 1-octene, and, to a much lesser extent, 4-methyl-1-pentene (a propylene dimer) (Section 6.3) as comonomers.

1-Butene for LLDPE may be obtained either by dimerization (Section 5.3.1) or oligomerization (Sections 5.3.2 and 5.3.3) of ethylene or by isolation from the C_4 olefin stream from steam or catalytic cracking (Chapter 7). In fact practically all of it in the United States and Western Europe is obtained from the latter source, which underscores the point that refinery processes usually are more economical than processes in chemical plants. Saudi Arabia makes 1-butene by dimerization of ethylene (Section 5.3.1) since refinery 1-butene is not available. 1-Hexene and 1-octene are obtained solely by ethylene oligomerization and 4-methyl-1-pentene by propylene dimerization (Section 6.3). Growth has been particularly rapid for the copolymer containing 1-hexene.

5.1.5 Very High Molecular Weight Polyethylene

Very high molecular weight polyethylene with a density of 0.941 g/cm^3 or higher is not used widely because it is difficult to process. It is made under high density polyethylene conditions without comonomer and is used primarily for plastic ropes. A low volume but growing application is for the preparation of high strength polyethylene fibers. Tensile strength in polymeric fibers may be increased by drawing, a process that causes the polymer molecules to crystallize or to align themselves so closely that physical forces of attraction between polymer molecules come into play. However, physical stretching does not cause uncoiling of small portions of molecules which are “tangled” because of folds and crossovers. It has been found that polymer molecules uncoil in very dilute solution if the solvent has high solvating power and the polymer is nonpolar. DSM have developed a process in which a dilute hydrocarbon solution of very high molecular weight polyethylene at 120°C is cooled to give a gel that is extruded into gel-like fibers. The solvent is removed and replaced with dichloromethane, which effects more unraveling. The second solvent is then removed and the dry gel oriented or drawn to provide a fiber, trade named Dyneema, whose tensile strength is fifteen times as great as that of steel on a weight for weight basis and 40% greater than Aramid fibers (Section 11.3.4). An obvious disadvantage of polyethylene fibers is their low melting point as compared with Aramids. On the other hand they absorb less water. Cloth from these fibers is used in body armor, ropes, cables, nets, and sports goods.

Very high molecular weight polyethylene is also used for the bottoms of skis. These must be abrasion resistant and hydrophobic and absorb wax well. PTFE (Section 12.2.3) would be ideal but is subject to creep. The cheaper skis use polyethylene with a molecular weight of about 500,000 and a density of 0.95 g/cm^3 . The molecular weight is just low enough for the bottoms to be extruded from the melt. Racing skis use polyethylene with a molecular weight of about 3.5 million and a density of about 0.94 g/cm^3 . They are formed by sintering the polymer into a block and then slicing it. This gives them a slightly porous structure leading to higher wax absorption and abrasion resistance. Sintering does not always produce uniform materials and various additives may improve this. Graphite or carbon black is often added, which makes the bases more conductive and decreases the effect of static

electricity on snow adhesion. Ski manufacture is a classic example of adding value to a few kilograms of polyethylene.²

5.1.6 Metallocene Polyethylenes

As described in detail in Section 17.3.12, metallocene catalysts, in contrast to conventional Ziegler–Natta catalysts, are discrete compounds and have single active catalytic sites. As a result, polyethylenes made using metallocene catalysts have a narrow molecular weight distribution and comonomers are incorporated in the polymer chain in a uniform manner. This gives the resulting polymer improved properties, including lower crystallinity, greater clarity, and lower heat seal temperatures. On the downside, metallocene-based polyethylene is typically more expensive than Ziegler–Natta-based polyethylene and can be more difficult to process.

5.1.7 Very Low Density Polyethylene

Very low density polyethylene (VLDPE) is defined by a density range of 0.880–0.915 g/cm³. It is a substantially linear polymer with high levels of short-chain branches, commonly made by copolymerization of ethylene with about 10% of short-chain α -olefins (e.g., 1-butene, 1-hexene, and 1-octene) used for the preparation of LLDPE. It is most commonly produced using metallocene catalysts (Section 17.3.12) because of the greater comonomer incorporation exhibited by these catalysts. The material is suitable for “noiseless” film of the type needed in adult diapers and other applications where low stiffness coupled with reasonable strength is required.

5.1.8 Bimodal HDPE

Most HDPE resins are based on unimodal (single reactor) process technologies and have performed well for many decades (Section 5.1.3). However, the emergence of new applications with more severe operating requirements has pushed the performance demands on HDPE resins to new levels. As a result, “bimodal” HDPE was established to improve some aspects of performance lacking in unimodal HDPE.

Bimodal resins are essentially the combination of high and low molecular weight polymers, each with its particular weight average and distribution. Compared with traditional unimodal HDPE, bimodal resins yield broader range of molecular weight distribution and high performance characteristics, leading to greater product design flexibility.

Molecular weight distribution (MWD) is dependent on the type of process used to manufacture the polymer. Using one catalyst in one reactor generally produces unimodal HDPE resins. Normally, bimodal resins are produced by two polymerization reactors in series, each operated under different process conditions to yield low and high molecular weight polymers. The ratio of the high and low molecular weight fractions is adjusted to balance the resin’s properties. Resins with bimodal MWD,

containing two peaks of short and long polyethylene chains, therefore have a wide molecular weight distribution, which gives excellent physical properties, while maintaining good processability. Indeed, the high molecular weight fraction provides good mechanical properties, such as high impact resistance, high tensile strength, and high environmental stress crack resistance (ESCR), while the low molecular weight fraction acts as a lubricant to provide good processability. Sequential polymerization also allows the control of comonomer distribution to incorporate very few branches in the lower molecular weight fraction and more branches in the higher molecular weight fraction.

A major development thrust for HDPE has been into bimodal grades for high performance film, pressure pipe, and to a lesser extent blow molding applications. Bimodal products have better processability, without loss of mechanical strength. This permits downgauging and a reduction in product profile or thickness. For film, the same area of film can be made with less polymer, while for pressure pipes, reduced wall thickness reduces raw material requirements and makes a more flexible pipe.

One important trend in the HDPE market is the increased number of bimodal-capable plants. Bimodal technology innovations resulted in improvement of existing technologies, such as LyondellBasell's Hostalen™ and Mitsui's CX processes. Currently, most commercial bimodal polyethylene is produced in multiple reactor configurations, particularly dual reactor processes, which are optimal for the tailoring of resin structure. Univation (Dow/ExxonMobil) has recently successfully completed its bimodal production technology in a Unipol single reactor. (See Nexant Chem-Systems POPS report, Supplement I, Bimodal HDPE, February 2009.)

5.1.9 "Green" Polyethylene

Photodegradable "green" ethylene copolymers are discussed in Section 19.12. In 2007, Braskem in Brazil produced development quantities of HDPE using ethylene made by dehydrating sugar cane-based ethanol. Braskem has labeled this plastic as "green" polyethylene. Although there is no hard and fast definition for a "green" product, and the Braskem polyethylene does not meet one of the usual goals of an environmentally friendly product, since the polymer is not biodegradable, it can be thought of as green since it is made from a renewable resource.

Dehydration of ethanol to ethylene is not a new idea and has been used in India for many years to make small volumes of ethylene. This approach is now being revisited but with a different perspective. The price of crude oil rocketed to over \$100/barrel in 2007 and frequently afterwards. Interest in bio-based feedstocks increased both because of their cost and environmental friendliness. When oil prices relax (but they are high at the time of writing), some of this interest fades. Braskem, with access to low cost sugar cane-based ethanol in Brazil, is continuing this development effort, and in 2008 produced green LLDPE. In addition to using green ethylene from ethanol, Braskem made the 1-butene comonomer by dehydrating biobutanol.³ Braskem brought online a 200,000 metric ton per year green LLDPE plant in September 2010.⁴ BP is building a similar plant for bioethanol and biobutanol at

Hull.⁵ The traditional route to biobutanol – the corn-based Weizmann process – gives poor yields (about 8% acetone and 16% butanol). It will be discussed further in Section 16.6.

5.2 ETHYLENE COPOLYMERS

5.2.1 Chlorosulfonated Polyethylene

Ethylene is found in many other copolymers in addition to HDPE and LLDPE, but all of them are sold in comparatively low volumes. One of the earliest is chlorosulfonated low density polyethylene, known as “Hypalon.” It is an elastomer formed by chlorosulfonation of polyethylene with sulfur dioxide and chlorine leading to insertion of SO_2Cl and Cl groups into the chain. For the various grades of Hypalon, LDPE, LLDPE, and HDPE may be used. This is a rare example of polymer modification by a chemical reaction in which the polymer is one of the reactants. The polymer can be crosslinked through the sulfonyl chloride group (which has destroyed the polymer’s crystallinity and made it rubbery) with inorganic oxides such as lead oxide or with di- or polyamines. This elastomer is prized because of its ozone and oxidation resistance. It finds use in gaskets, wire and cable installation, roof coatings, white sidewall tires, and coated fabrics.

5.2.2 Ethylene-Vinyl Acetate

The most important ethylene copolymer after HDPE and LLDPE is ethylene-vinyl acetate (EVA). Its consumption was approximately 1.9 million metric tons in 2009, which is about 75% of all ethylene copolymers excluding HDPE and LLDPE. Ethylene-vinyl acetate is a random copolymer. Depending on the proportion of vinyl acetate, it may be either hard or rubbery.

The hard form requires less than 50% of vinyl acetate. Like most copolymers, it has a lower density than the homopolymer and is useful in agricultural films because it demonstrates better heat retention, toughness, and greater transparency, trapping more infrared light than does LDPE. Its biggest use is for adhesives, particularly hot melts, where the adhesive is applied as a solvent-free melt and bonds almost instantaneously on cooling. It is used as a coating often blended with waxes, polyolefins, and elastomers. An interesting medical application is as a semipermeable film for drugs administered in sustained release dosage forms. A drug such as trinitroglycerol is placed in a reservoir covered with the semipermeable film, which in turn is placed next to the skin. The drug enters the body since the skin too is semipermeable, and it makes its way into the bloodstream at a controlled rate via the semipermeable capillaries.

If more than 50% vinyl acetate is present, a rubbery polymer results, which in the form of a latex is useful for water-based paints along with other homo- or copolymers of vinyl acetate, acrylates, and methacrylates. The ethylene lowers the cost of the polymer and contributes much-prized water resistance.

Related copolymers include ethylene-ethyl acrylate, ethylene-methylacrylate, ethylene acrylic acid, ethylene-butyl acrylate, and ethylene-methacrylic acid. Each of these has properties that fit it for specific uses. For example, ethylene-ethyl acrylate is used mainly as a cable coating. Ethylene-butyl acrylate provides a tough film with excellent low temperature properties, fitting it for the packaging of frozen foods. The ethylene-ester copolymers can be made in either LDPE autoclaves or tubular reactors. The ethylene-acid copolymers are typically made in an autoclave reactor.

Ethylene-vinyl alcohol is a copolymer prepared by conversion of the ester groups of ethylene-vinyl acetate to alcohol groups by ester interchange with methanol. Its films are good oxygen barriers and, because of its high polarity, it has good resistance to oils and greases. The copolymer was developed in Japan; U.S. manufacture started in 1986. Laminates may be made by coextrusion of ethylene-vinyl alcohol copolymer with other polymers such as polyethylene, polypropylene, or polyesters such as poly(ethylene terephthalate) (PET). Ethylene-vinyl alcohol/PET and ethylene-poly(vinylidene chloride)/PET laminates are less permeable to oxygen and carbon dioxide than PET alone and are being used for smaller beer bottles in the international market (Section 11.3.3).

5.2.3 Ionomers

Ethylene-acrylic acid and ethylene-methacrylic acid are examples of random copolymers. They are useful as such and also in the preparation of ionomers. Ionomers comprise a class of copolymers of which DuPont's "Surlyn" is typical. An ionomer contains ionic groups such as pendant carboxyl groups. These react with both divalent and monovalent metal ions such as Zn^{2+} and Na^{+} to crosslink the polymer chains by the formation of carboxylates. The monovalent ion is effective because of the formation of ion aggregates through coulombic forces. The hygroscopic aggregates attract water even in a medium as nonpolar as an ethylene-containing polymer. The water serves to stabilize the aggregate and makes possible the reversal of salt formation on heating.

The virtue of an ionomer is that it has some of the stiff, tough properties of a crosslinked resin at room temperature. On heating, the ionic bonds or ion aggregates are disrupted and the polymer becomes thermoplastic and processible. Major uses for ionomers include ski boots, tough, flexible hosing, and the coating of golf balls, where toughness is a major requirement. Very tough forms of ionomers have been proposed for body panels and bumpers of automobiles. It is also used for specialty packaging.

5.2.4 Copolymer from "Incompatible" Polymer Blends

Polar polymers such as nylon are incompatible with nonpolar polymers such as polyethylene for the same reasons that polar and nonpolar liquids are immiscible. They can, however, be combined in an imaginative process, which uses a third polymer.⁶ The technique is exemplified by DuPont's "Sclar."

Sclar is a blend of nylon and ethylene plus a graft copolymer of ethylene and acrylic or methacrylic acid. The copolymer serves as a "nail" to hold the incompatible

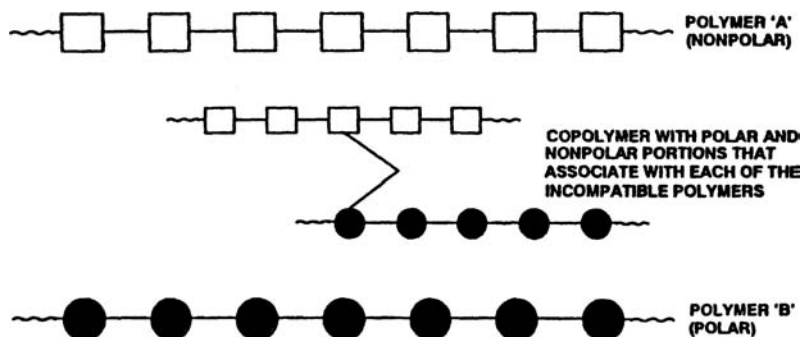


FIGURE 5.4 A chemical “nail” holds two incompatible polymers together.

polyethylene and nylon together. Its polar portion, the pendant carboxyl groups, associate with the nylon and may even react chemically with amine end groups. The polyethylene backbone of the copolymer, on the other hand, associates with the polyethylene homopolymer. These physical bonds are sufficiently strong to prevent phase separation and accordingly the nylon, which is the lesser component, “plates out” in the polyethylene matrix when the molten mixture is cooled. The nylon platelets overlap, providing a barrier that makes the blend suitable for structures where good oil resistance is required. One use is for the fabrication of automotive fuel tanks. Figure 5.4 illustrates this important concept for combining incompatible polymers.

5.2.5 Ethylene–Propylene Elastomers

Ethylene–propylene copolymers containing 20–80% ethylene are noncrystalline elastomers, which can be crosslinked with peroxide. Alternatively, a diene may be included such as *trans*-1,4-hexadiene (Section 7.1.5), ethylidene norbornene (Section 5.1.2), or dicyclopentadiene (Section 8.3), each of which contains one active double bond to copolymerize with the ethylene and propylene and one less reactive pendant double bond for crosslinking of the rubber with conventional sulfur-based vulcanizing agents. The polymerization is carried out with a Ziegler catalyst. Because only enough double bonds are present to permit crosslinking, the polymer is particularly stable and resistant to oxidation. These elastomers find specialty uses where long service life is required, particularly for roofing. They are also used in automobiles for gasketing, belts, hose, wire and cable coating, and under-the-hood applications where high temperature resistance is required. They may be used to reinforce other polymers.

5.2.6 Polyolefin Elastomers

Polyolefin elastomers (POEs) are copolymers of ethylene and an alpha olefin. POEs contain about 65% ethylene and 35% octene-1, hexene-1, or butene-1. The metallocene catalyst selectively polymerizes the ethylene and comonomer sequences.

By increasing the comonomer content, it will produce polymers with higher elasticity, as the comonomer incorporation disrupts the polyethylene crystallinity. Furthermore, the molecular weight of the copolymer will help determine its processing characteristics and end use, with higher molecular weights providing enhanced polymer toughness.

POEs are a new class of polymers that emerged from advances in metallocene catalysts. Representing one of the fastest growing synthetic polymers, POEs can be substituted for a number of generic polymers including ethylene–propylene rubbers (EPR or EPDM), ethylene-vinyl acetate (EVA), styrene-block copolymers (SBCs), and poly(vinyl chloride) (PVC).

POEs can be thermoplastic or thermosetting, the latter by crosslinking with peroxide catalysts. They are compatible with most olefinic materials, are an excellent impact modifier for plastics, and offer unique performance capabilities for compounded products. They have been used as low-cost rubber replacements for some nondemanding molded goods applications, such as those that will not be exposed to extremes in temperatures, pressures, loads, or stress environments. In molded goods, POEs are being used where “some” degree of flexibility or tactile feel is desired.

5.3 OLIGOMERIZATION

Ethylene oligomerizes with difficulty because the free radical intermediate, once formed, is highly energetic and polymerizes rapidly to give high molecular weight polymers. Thus it was not until the advent of Ziegler technology that ethylene oligomerization became feasible. Conversely, ionic intermediates from propylene and butenes form readily. Since they are much less energetic, they oligomerize, but do not polymerize.

5.3.1 Dimerization

Ethylene may be dimerized either to 1-butene or to the more thermodynamically stable 2-butene. The original incentive for the development of dimerization processes was the possibility of dehydrogenating the resulting butenes to butadiene just as refinery butenes are dehydrogenated (Section 4.12). Although, this concept was never commercialized, the current trend to use lighter and cheaper feedstocks in steam crackers is causing a butadiene shortage, and new “on-purpose” routes to butadiene are under development (Chapter 7). This in turn could stimulate renewed interest in ethylene dimerization to butenes.

Dimerization has already been mentioned in Section 4.14. Dimerization to 1-butene was first commercialized on a large scale (50,000 metric tons per year) by SABIC in Saudi Arabia, where this chemical was needed for use in LLDPE. Saudi has limited amounts of butenes, normally obtained from naphtha crackers. This process, termed ALPHABUTOL[®], was jointly developed by SABIC and Axens and is based on a titanium catalyst. The inventors propose that the catalyst goes through a titanium cyclopentane intermediate which decomposes to 1-butene by intramolecular

hydrogen transfer. Another possibility, never commercialized, is the production of 1-butene in situ before or during ethylene polymerization to provide the comonomer needed for LLDPE (Section 5.1.4).

5.3.2 Ziegler Oligomerization of Ethylene

Related to Ziegler polymerization is the oligomerization of ethylene as shown in Figure 5.5. Triethylaluminum reacts with ethylene to form a trialkylaluminum at 100°C and 100 atmospheres. An aluminum alkoxide results from the interaction of the trialkylaluminum with oxygen. It can be hydrolyzed to straight-chain fatty alcohols with an even number of carbon atoms from C₄ to C₂₄. Alternatively, the trialkylaluminum may be heated to 280–300°C and 50 bar in the presence of ethylene to give linear α -olefins. Both groups of compounds are useful in the manufacture of biodegradable detergents, but the alcohols are much more widely used. The α -olefins are converted to alcohols with one additional carbon atom by use of the oxo reaction (Section 6.9). The C₁₀ α -olefins may in turn be oligomerized to trimers to obtain compositions valuable as synthetic lubricants, and the C₁₈ compounds may be sulfonated to obtain both industrial-grade and specialty surfactants useful in cosmetics. The C₆ and C₈ olefins are useful as comonomers for LLDPE (Section 5.1.4).

This technology was adopted by several companies. The major problem with the process is an unfavorable molecular weight distribution of the products, which ranges from C₄ to C₂₄. Conoco (spun off as Vista, now owned by Sasol) produced the alcohols whereas Ethyl (now Ineos) and Gulf (now Chevron-Phillips Chemical) produced α -olefins. The most desirable materials for surfactants contain 12–14 carbon atoms. A process developed by the Ethyl Corp. recycles α -olefins to the chain growth step so

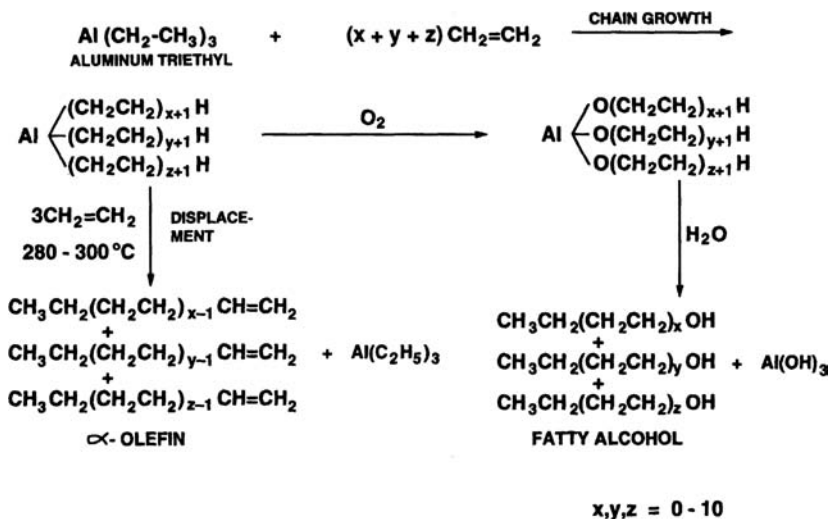


FIGURE 5.5 Ethylene oligomerization (Ziegler).

that transalkylation takes place. This gives a higher concentration of C_{12} – C_{18} compounds and fewer of the lower molecular weight materials, although it introduces some branching. The displacement is effected by raising the temperature to 300°C. The alkylaluminums with chain lengths from 12 to 18 are replaced by the lower molecular weight olefins that form at the high temperature. This provides alkylaluminums with chain lengths of 4–12 and free C_{12} – C_{18} α -olefins. In other words, the displacement reaction shown in Figure 5.5 is allowed to take place in situ rather than as a separate step, using C_4 – C_{12} α -olefins to displace the alkyl chains rather than ethylene. High pressure favors chain growth since it reduces the number of molecules. Displacement, on the other hand, as indicated above, is favored by high temperature. The effectiveness of the transalkylation reaction is indicated by the fact that C_{12} – C_{14} α -olefin production is increased from 10–18% to 20–35%.

The equations in Figure 5.5 show that the reaction requires stoichiometric quantities of triethylaluminum. However, it is possible to carry it out with catalytic amounts if the conditions are such that ethylene continually displaces the growing chains on the catalyst. β -Hydrogen abstraction from the growing alkyl chain regenerates an Al–H bond that can start growth of a new alkyl chain. When alcohols are made, stoichiometric amounts of $Al(OH)_3$ are formed. This may be converted to a high-value catalyst support.

α -Olefin technology may now be licensed from UOP, Axens (formerly IFP), or SABIC/Linde. The UOP process, Linear-1™, was developed jointly with Union Carbide. It employs a homogeneous nickel-based catalyst system. While many ligand combinations were tested, it appears that 2-diphenylphosphino-1-naphthalene sulfonic acid is used. UOP claims that, by making simple adjustments to the operating parameters, the output can be varied between 45 and 75 weight percent C_4 to C_8 linear α -olefins. The Axens process, AlphaSelect®, is based on a proprietary soluble catalyst system. Varying the catalyst and cocatalysts ratio allows different α -olefin distributions. The process jointly developed by SABIC and Linde is called Alpha-SABLIN® and is based on a zirconium/aluminum catalyst. The process hinges on a unique bubble phase reactor. It is claimed that this reactor allows for a simple process design and moderate reaction conditions. SABIC built a 150,000 metric ton per year α -olefin plant using this process in Jubail, Saudi Arabia, in 2006.

5.3.3 Other Ethylene Oligomerization Technologies

The chromium-catalyzed trimerization of ethylene to 1-hexene is a remarkable reaction devised by Phillips Petroleum. In the early 2000s Chevron–Phillips, in a joint venture with Qatar Petroleum (Q-Chem), built a 47,000 metric ton per year 1-hexene plant in Qatar as a comonomer for LLDPE. The proposed mechanism is shown in Figure 5.6.⁷ The original chromium complex, designated as “Cr,” specifying the actual ligand system which is proprietary, binds first one and then a second ethylene molecule to give a five membered chromium-containing ring. Five membered rings are thermodynamically relatively stable, and this one remains intact long enough to bond to another ethylene molecule to give a complex that rearranges to a seven membered ring. Seven membered rings are relatively unstable and this one

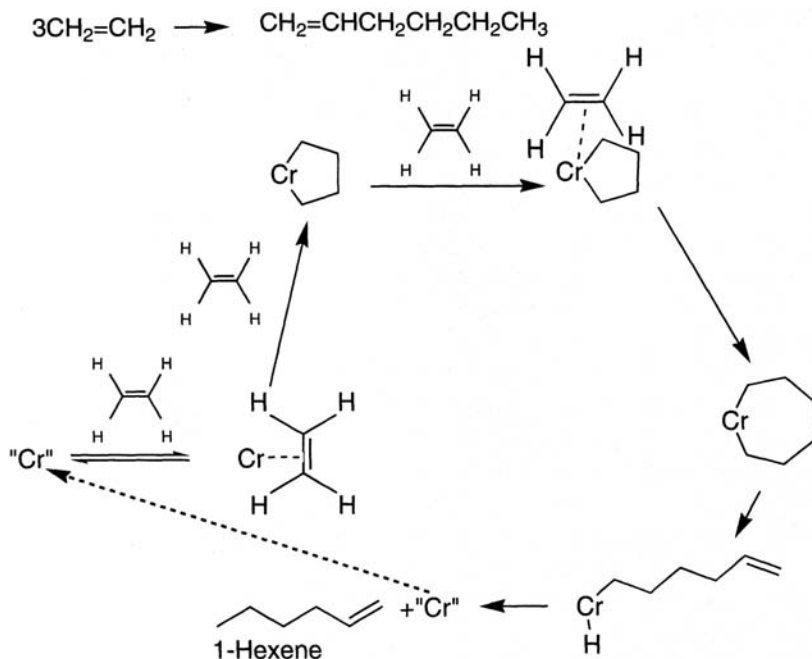


FIGURE 5.6 Trimerization of ethylene to 1-hexene.

decomposes via ring opening and reductive elimination to give 1-hexene and the original chromium starting complex.

Researchers at Sasol have found a catalyst system and operating conditions that allow, indeed favor, formation of the nine membered metallacycle in relation to the seven membered ring as described above. This provides a fairly selective reaction to octene-1.

The Sasol catalyst is an aluminoxane-activated chromium/ $((\text{R}^2)_2\text{P})_2\text{NR}^1$ system. A number of diphosphino ligands with various substituents on both the N and P have been evaluated. All catalysts gave good selectivity for octene-1 and varying quantities of hexene-1, along with other cyclic C_6s such as methylcyclopentane and methylene cyclopentane. Relatively small amounts of $\text{C}_{10}\text{--C}_{16}\text{s}$ and polymer are also formed. The use of modified methylaluminoxane (MMAO) as an activator leads to substantially higher overall yields.

Sasol has postulated two mechanisms⁸ to account for the high selectivity to octene-1.

In Pathway A, ethylene is inserted and expands the metallacycloheptane to a metallacyclononane. This nine membered ring then decomposes to octene-1. Alternatively, Pathway B shows beta-hydride transfer from the metallacycloheptane to a coordinated ethylene to give a hexenyl ethyl Cr species and reductive elimination to give octene-1. These mechanisms imply a competition between the metallacycloheptane decomposing to hexene-1 and expanding to the metallacyclononane and then decomposing to octene-1. This is consistent with lower temperatures seeming to favor

more octene-1, as at higher temperatures the nine membered metallacycle becomes too unstable.

Sasol has built three plants at Secunda, South Africa, with a combined capacity of 190,000 metric tons and is planning to build a commercial unit in the United States using this new catalyst system. It will have a capacity of 100 thousand metric tons per year of 1-octene and 1-hexane and is slated to start up in 2013.⁹

Sasol is deeply involved with α -olefins and also obtains them from its synthetic fuel plant described in Section 14.2.

5.3.4 Shell Higher Olefins Process (SHOP)

Shell devised a process, which is integral to their SHOP process, based on a nickel chloride catalyst with ligands comprising diphenylphosphinoacetic acid and triphenylphosphine. Sodium borohydride is present to reduce the nickel salt to a nickel hydride catalyst, and a glycol such as 1,4-butanediol serves as a solvent for the reactants but not the products.

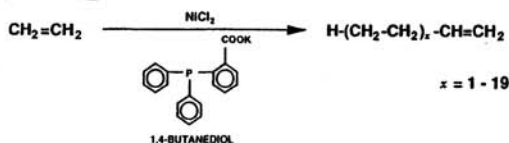
The oligomerization takes place at about 100°C and 40 bar in the presence of excess ethylene. The mixture of α -olefins that forms has chain lengths varying from C_4 to C_{40} . The distribution includes 40.5% of C_{10} – C_{18} α -olefins, 41% C_4 – C_8 compounds, and 18.5% of C_{20} and higher materials. The α -olefin distribution is similar to that obtained in a Ziegler process carried out without transalkylation. The mechanism of α -olefin formation, like the one for the alkylaluminum reaction, involves β -hydrogen abstraction as shown in Section 5.3.2. The product α -olefins precipitate because they are not soluble in the 1,4-butanediol.

The SHOP process is one of the most ingenious in the chemical industry.¹⁰ Its initial objective was the preparation of linear or almost linear α -olefins and fatty alcohols with the most suitable chain lengths for surfactants, that is, C_{11} – C_{15} . The natural products – coconut and palm kernel oils, from which fatty alcohols may be prepared (Section 15.8) – provide C_{12} and C_{14} chain lengths, but a carbon more or less is also acceptable. The SHOP process comprises a combination of four reactions, each of which was already known, at least in concept, although some required modification. Thus it is an excellent example of that form of creativity that involves the reordering of old knowledge to achieve a new end result.

As shown in Figure 5.7, the first step in the process is the oligomerization of ethylene as described in Section 5.3.3. A spread of chain lengths is obtained with a “bell-shaped” statistical distribution. The processes can be engineered so that the peak of the distribution is at C_{10} – C_{14} and these α -olefins comprise about 30% of the reaction mixture, which means that approximately 70% of unwanted chain lengths is produced.

From the C_4 – C_{40} mixture of α -olefins, C_{10} – C_{14} products are separated by distillation (Step 2, Fig. 5.7). Any other chain length may also be removed by fractionation should a market exist for it. The C_{10} – C_{14} α -olefins are hydroformylated (Step 3, Fig. 5.7) to C_{11} – C_{15} alcohols. Linear hydroformylation normally requires a rhodium catalyst (Section 6.9), which is best recovered by distilling the product to leave the expensive rhodium in the vessel.

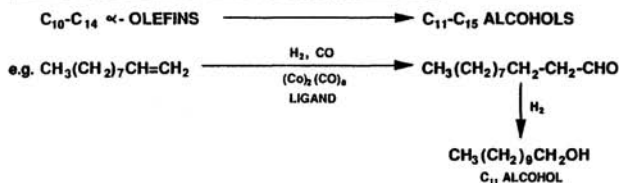
1. OLIGOMERIZATION



2. FRACTIONATION OF α -OLEFINS

- a. C_{10} - C_{14} α -OLEFINS
- b. C_4 - C_8 α -OLEFINS
- c. C_{16} - C_{40} α -OLEFINS

3. LINEAR HYDROFORMYLATION OF C_{10} - C_{14} α -OLEFINS

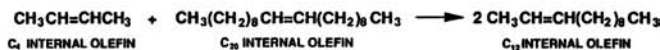


4. ISOMERIZATION

- a. C_4 - C_{10} α -OLEFINS \longrightarrow C_4 - C_{10} INTERNAL OLEFINS
 - b. C_{16} - C_{40} α -OLEFINS \longrightarrow C_{16} - C_{40} INTERNAL OLEFINS
- e.g. $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \longrightarrow \text{CH}_3\text{CH}=\text{CHCH}_3$
- $$\text{CH}_3(\text{CH}_2)_{17}\text{CH}=\text{CH}_2 \longrightarrow \text{CH}_3(\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_8\text{CH}_3$$

5. METATHESIS OF C_4 - C_8 AND C_{16} - C_{40} INTERNAL OLEFINS

SHORT AND LONG CHAIN INTERNAL OLEFINS
DISPROPORTIONATE



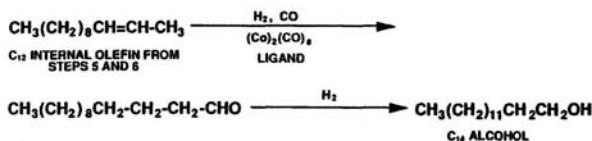
6. FRACTIONATION OF INTERNAL OLEFINS

a. C_{10} - C_{14} INTERNAL OLEFINS

b. C_4 - C_8 INTERNAL OLEFINS

c. C_{16} - C_{40} INTERNAL OLEFINS

7. LINEAR HYDROFORMYLATION OF C_{10} - C_{14} INTERNAL OLEFINS



8. REPEAT STEPS 5, 6, AND 7 TO EXTINCTION

FIGURE 5.7 Shell higher olefins process (SHOP).

Shell's products have too high molecular weights to allow for rhodium recovery in this way. More important, the rhodium catalyst does not shift the double bond to the α -position as is required later in the process. Accordingly, Shell uses a dicobalt octacarbonyl catalyst with ligands such as tributylphosphine. This catalyst has the even more important advantage of making possible the linear hydroformylation of internal olefins, as will be seen later. From the C_{10} – C_{14} α -olefins, linear alcohols result with chain lengths of 11–15 carbon atoms.

In the fourth step (Fig. 5.7) the C_4 – C_{10} and the C_{16} – C_{40} α -olefins are isomerized to internal olefins using heterogeneous catalysts such as magnesium oxide granules. Isomerization takes place at 80–140°C and 4–20 bar. Internal double bonds are distributed randomly throughout the olefin molecules.

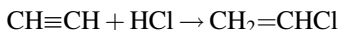
The next step (Step 5 in Fig. 5.7) involves metathesis (Section 4.14) of the short- and long-chain internal olefins to provide new internal olefins with a broad distribution of chain lengths, some of which are in the desired C_{10} – C_{14} range. The example shows a metathesis reaction between a C_4 and a C_{20} internal olefin to yield two molecules of a C_{12} internal olefin. The desired chain lengths are removed by distillation, 10–15% being obtained (Step 6 in Fig. 5.7). These internal olefins are again subjected to linear hydroformylation as shown in Step 7, using the above-described cobalt octacarbonyl catalyst, which causes the migration of the double bond to the α -position. The intermediate aldehydes, which are produced by hydroformylation, are hydrogenated in situ.

Step 6 provides further quantities of C_4 – C_8 and C_{16} – C_{40} internal olefins and these again are subjected to metathesis. Thus Steps 5, 6, and 7 are repeated to extinction. High yields are obtained in each step.

The process is versatile. Thus C_6 and C_8 olefins may be removed for sale to LLDPE manufacturers (Section 5.1.4) and the C_{10} olefin may be isolated for use in synthetic lubricants. In this case, only the C_4 olefin is used in the metathesis reaction, and if necessary more can be obtained from steam or catalytic cracking (Section 4.6). The internal olefins may be sold for the alkylation of benzene (Section 9.4) for surfactants. There were two SHOP plants in operation in 2003, one in Geismar, Louisiana, and another in Stanlow, UK. The initial capacity was 104,000 metric tons/year but has been repeatedly expanded and is approaching a million tons. Other plants are planned.

5.4 VINYL CHLORIDE

Vinyl chloride (VCM) is the monomer for poly(vinyl chloride). Originally it was made by addition of hydrogen chloride to acetylene:



The acetylene route fell out of favor for safety and economic reasons and was superseded by ethylene-based processes described below. Recently, the acetylene route has made a comeback in China, and this will be described in more detail at the end of this section.

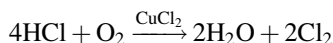
Ethylene-based vinyl chloride was first made by production of ethylene dichloride from ethylene and chlorine which, when heated in contact with pumice or charcoal, yielded vinyl chloride and a mole of HCl:



The by-product presented a problem, for hydrogen chloride is corrosive and difficult to ship. Unless it can be used on site, its value is small. Disposal presents economic and environmental problems. Furthermore, half the chlorine (produced by electrolysis, which requires expensive electrical energy) was wasted.

One solution was to react the by-product hydrogen chloride with acetylene in a second plant. In this way, the chlorine was saved but, as the price gap between ethylene and acetylene widened, the process (the so-called integrated chlorine economy) became less attractive and a wholly ethylene-based process became desirable.

The first approach involved resurrection of a Victorian process. In 1858 Deacon had shown that hydrogen chloride can be oxidized to chlorine by air over bricks soaked in copper chloride. It was the first heterogeneous catalytic process to be operated.

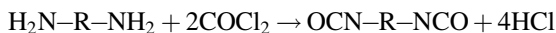


Shell investigated the reaction and improved the catalyst. The snag was that the hydrogen chloride had to be isolated and oxidized and the chlorine separated and recycled. Before the process could be instituted, a related process was developed called oxychlorination. No one, except DuPont briefly, used the modernized Deacon process; its value lies in the fact that it led to oxychlorination. Oxychlorination is typical of modern petrochemical processes whose aim is to pass a simple feedstock through a hot tube over an appropriate catalyst, with the desired chemical emerging at the end. Of course, the secret lies in the “appropriate” catalyst.

In oxychlorination, the Deacon chemistry was incorporated into a one-step reaction in which 1 mol of ethylene, 2 mol of hydrogen chloride, and air are passed over a copper chloride/potassium chloride catalyst to give ethylene dichloride. This is mixed with the ethylene dichloride from the chlorination process and cracked to vinyl chloride and by-product hydrogen chloride, which is returned to the oxychlorination process (Fig. 5.2e). Unless there is a separate source of by-product hydrogen chloride, the chlorination and oxychlorination plants are integrated and half of ethylene dichloride production is made by chlorination and half by oxychlorination. The two reactions are necessary since each provides a mole of hydrogen chloride. Together, this gives the 2 mol that oxychlorination requires.

This was the dominant process for many years, but a more modern approach is to make use of the hydrogen chloride produced in isocyanate manufacture (Sections 9.3.1 and 10.3) to supplement supplies from the chlorination step of the integrated process. The reaction of a diamine with phosgene and its subsequent cracking to a diisocyanate

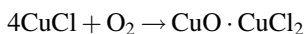
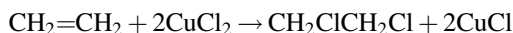
(the most important route to isocyanates) generates four molecules of hydrogen chloride:



If the hydrogen chloride was not used for oxychlorination, it would present a disposal problem. It is corrosive and cannot be stored or shipped by conventional means. It can, however, be transmitted by pipeline to a vinyl chloride unit, and most isocyanate manufacturers do this.

The direct chlorination of ethylene is generally carried out in the liquid phase with the product ethylene dichloride as the reaction medium and with dissolved FeCl_3 , CuCl_2 , or SbCl_3 as catalyst at 40–70°C and 4–5 bar.

Oxychlorination is a gas phase reaction taking place at about 225°C and 2–4 bar with a cupric chloride catalyst supported on alumina or silica together with potassium chloride, whose chloride ion serves as an activator. The cupric chloride is the chlorinating agent. It chlorinates the ethylene and is itself reduced to cuprous chloride. Oxygen regenerates the cuprous chloride by converting it to a double salt of cupric oxide and cupric chloride. The double salt in turn reacts with the hydrogen chloride to give cupric chloride and water.



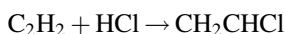
Because the reaction is highly exothermic, a fluidized bed reactor, which has much better heat transfer capability than a fixed bed, may be used. The chemical industry provides many examples of the use of fluidized beds for heat transfer as in acrylonitrile production (Section 6.5), catalytic cracking (Section 4.14), and vinyl acetate production (Section 5.6).

Vinyl chloride manufacture consumes about 20% of the chlorine produced in the United States. An objective of the chemical industry has been to devise routes to vinyl chloride and other C_2 compounds from ethane rather than ethylene.¹¹ Several processes have been devised but had not been commercialized by 2010. ICI (now INEOS) developed a vapor phase oxychlorination of ethane, which yielded vinyl chloride, water, and HCl. The catalyst comprised metallic silver with salts of manganese or lanthanum impregnated on an Offretite zeolite. Although conversions above 95% could be achieved, the selectivity to vinyl chloride was only about 50%. Other chlorinated products included ethylene dichloride and ethylene. The latter could be oxychlorinated in a separate operation. In the mid-1990s European Vinyl Corporation (EVC) announced they had developed a cost-effective process. The advantage of their technology was that the catalyst system was active at relatively low temperatures. This contrasts with most previous efforts, which required higher operating temperatures that led to severe corrosion problems. EVC built a 1000 ton per year pilot plant in Wilhelmshaven, Germany, but INEOS acquired EVC and has no

plans to commercialize this ethane-based route to VCM. The chemistry will be discussed in Section 13.2.1.

Another research aim for vinyl chloride production is to develop a process in which the overall reaction can be accomplished without isolation of the ethylene dichloride intermediate. The reaction conditions for the two steps, particularly temperatures, differ so widely, however, that satisfactory yields have not proved possible. Another possibility is the intermolecular dehydrogenation of ethylene and HCl in the presence of a reactant for the hydrogen produced. This is a thermodynamically feasible but elusive reaction.

The oldest and simplest commercial route to vinyl chloride monomer (VCM) is via the vapor phase addition of anhydrous hydrogen chloride to acetylene over a mercuric chloride (HgCl_2) catalyst supported on activated carbon:



The reaction is simple and of high yield when compared to other VCM processes, thereby allowing a simple product purification, and lower capital and operating costs. Over the past eight years, it has become an important process in China, and further expansion is planned. Currently, over 70% of Chinese VCM capacity is based on acetylene. There are three reasons for this. First, China has an abundance of coal and limestone; second, China lacks oil and ethylene; third, China has a long history of production of coal, coke, calcium carbide, and acetylene. China has much experience and significant R&D work in the process technologies and equipment. China's huge capacity growth now gives the acetylene-based route an estimated 20% share of the world's VCM capacity (Fig. 5.8).

On the downside, however, the production of carbide is energy and labor intensive. Its hydrolysis to acetylene produces huge quantities of a mercury-contaminated slurry of calcium hydroxide in water (Section 12.3). Thus this route is unattractive from a health and environmental perspective.

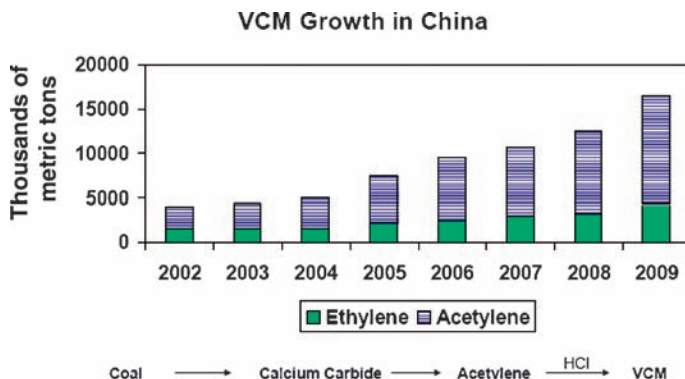


FIGURE 5.8 Growth of vinyl chloride monomer in China. (Source: Nexant Inc.)

The major use for vinyl chloride is for the manufacture of poly(vinyl chloride) (PVC) or copolymers (Chapter 17). It can be produced in rigid or flexible forms. The rigid form, which accounts for about 23% of consumption, is used for pipes, extruded profiles, thermoformed sheet, containers, and moldings. The flexible form is used for hoses, film/sheet, medical tubing and bags (because it can be sterilized at 120°C), flooring, electrical insulation of wiring, and coatings (Fig. 5.9). All PVC needs to be stabilized, primarily with metal salts of fatty acids or epoxidized soybean oil, but other processing aids are also added. Flexible PVC is compounded with plasticizers – di(2-ethylhexyl) phthalate is the most widely used (Sections 11.1.1) but is under attack by the environmental lobby. Adipates, sebacates, and all manner of lipophiles have also been used. Vinyl chloride is a starting material for vinylidene chloride, trichloroethylene, and tetrachloroethylene (Section 5.11.7). Ethylene dichloride, vinyl chloride's precursor, finds some application as a solvent, but use of most chlorine compounds in chemical processing is decreasing because of their persistence in the body. They are lipophilic and are not destroyed or excreted but are stored in body fat. Vinyl chloride monomer itself is toxic, causing angiosarcoma, a rare type of liver cancer. Accordingly, its concentration in ambient air during manufacture must be strictly limited. PVC is under attack because of possible migration of plasticizers, stabilizers, and pigments. It also gives rise to particularly unpleasant dioxins when inefficiently incinerated. There seems little evidence for the polymer itself causing ill effects.

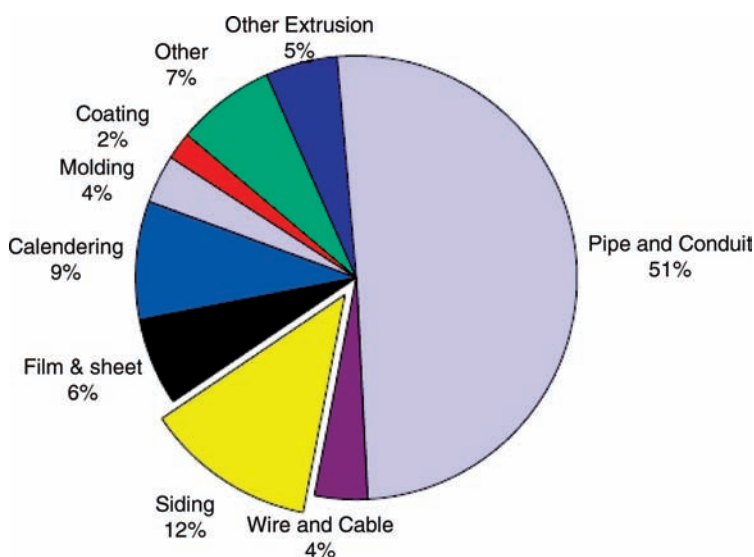


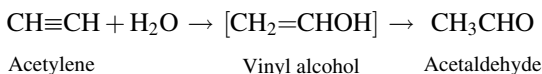
FIGURE 5.9 End-use pattern for PVC, United States, 2009. (Source: Nexant Inc.)

5.5 ACETALDEHYDE

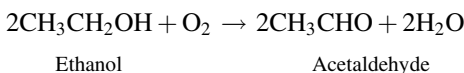
Acetaldehyde is one of the few industrial chemicals whose production has shrunk in the past 20 years. Its decline has been paralleled only by petrochemical ethanol (Section 5.9). In the United States in 1969, 30 million tons of acetaldehyde was manufactured. By the late 1980s this had decreased to an estimated 300,000 metric tons. Total world production in 2003 was about a million metric tons, a mere 3.3% of the earlier U.S. production.

Acetaldehyde was manufactured by an ingenious process, the Wacker reaction. Its demise was caused by the discovery of equally ingenious processes for the preparation of the two chemicals for which it served as precursor, *n*-butanol (Section 6.9) and, more important, acetic acid (Section 12.5.2.2). These three processes are examples of shutdown economics (see Appendix A). *n*-Butanol is no longer made by the old process but a little acetaldehyde may still be oxidized to acetic acid in Europe. Obsolete plants often still operate because the cash cost of operating them is lower than the total cost of the newer processes.

Acetaldehyde was originally made by the hydration of acetylene over an oxidation–reduction catalyst, mercurous/mercuric sulfate buffered by ferric sulfate. Vinyl alcohol is assumed to form momentarily and to rearrange to acetaldehyde at atmospheric pressure and 95°C.

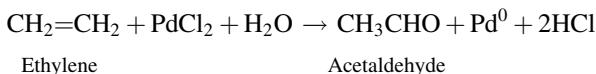


Ethylene became much cheaper than acetylene in the early 1960s and the above route was displaced by the oxidation of ethylene-based ethanol at 450°C and 3 bar with air over a silver gauze catalyst.



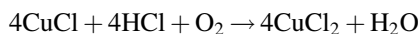
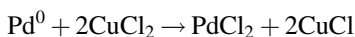
Alternatively, the ethanol may be dehydrogenated over a chromium oxide-activated copper catalyst at 270–300°C. This is a more attractive process if a use exists for the by-product hydrogen. By 1974 only 15% of acetaldehyde was made from acetylene.

These routes in turn gave way to the Wacker process described by Parshall as “a triumph of common sense.”¹² It is based on the observation that ethylene is oxidized by palladium chloride to acetaldehyde. As indicated, stoichiometric quantities of palladium chloride are required.

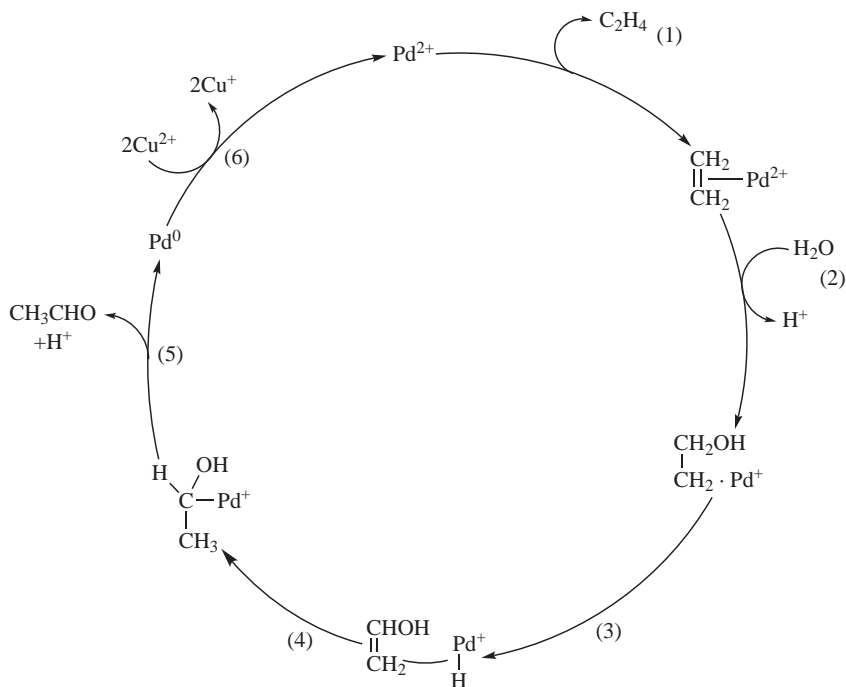


In the 1950s, chemists at Wacker Chemie in Germany converted the palladium salt from a stoichiometric to a catalytic component by including cupric chloride, oxygen,

and hydrogen chloride in the reaction mixture. Each atom of palladium, when formed, is then oxidized back to palladium chloride. The cuprous chloride is converted back to cupric chloride by oxygen:

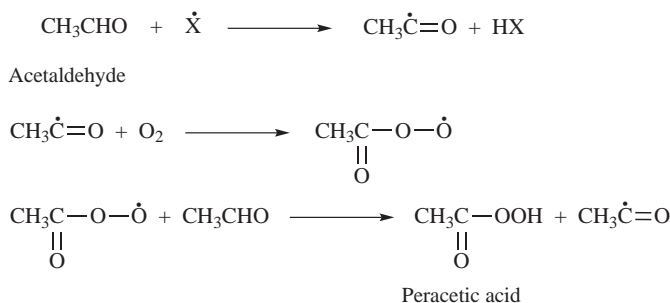


The mechanism proposed by Parshall (see notes) is shown in the following cycle:

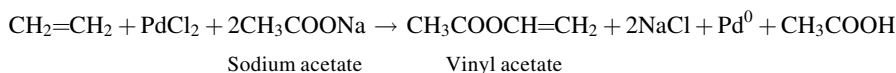


There is general agreement about the formation of the π -complex (Step 1). Step 2 is the OH addition. There is controversy as to how this step takes place. Thereafter the mechanism is straightforward, with hydrogen abstraction by the palladium (Step 3) followed by rearrangement (Step 4) and acetaldehyde formation (Step 5). The palladium chloride/copper chloride mixture is analogous to the oxychlorination system (Section 5.4).

n-Butanol (Section 6.9) was originally made from acetaldehyde by an aldol condensation (Section 5.11.3). Today it is made from propylene (Section 6.9) by hydroformylation. Acetic acid was made by oxidation of acetaldehyde with either air or oxygen over a manganese or cobalt acetate catalyst at 60°C. The oxidation takes place by a radical mechanism in which peracetic acid is the intermediate.



The modification of the Wacker reaction (Section 5.5) by substitution of acetic acid for water in the presence of potassium acetate yields vinyl acetate. Two processes were developed, one a homogeneous liquid phase reaction with a palladium chloride–cupric chloride catalyst, and the other a heterogeneous gas phase reaction with a $\text{PdCl}_2\text{--CuCl}_2$, $\text{PdCl}_2\text{--Al}_2\text{O}_3$ or palladium-on-carbon catalyst onto which a trickle of potassium acetate solution flows. Fixed and fluidized¹⁴ bed variants of the heterogeneous processes are in use.



The Pd^0 is regenerated by the CuCl_2 in the catalyst analogously to the conversion of Pd^0 to PdCl_2 in the acetaldehyde reaction (Section 5.5) except that the Cu^+ ion is converted to Cu^{2+} with air. No HCl is present since, together with the acetic acid, it is formidably corrosive.

The liquid phase process ran into severe corrosion problems from this combination. These might have been overcome, but there were also serious mass transfer problems because foaming in the reactor prevented sufficient ethylene from dissolving quickly enough, and thus the plant was closed.

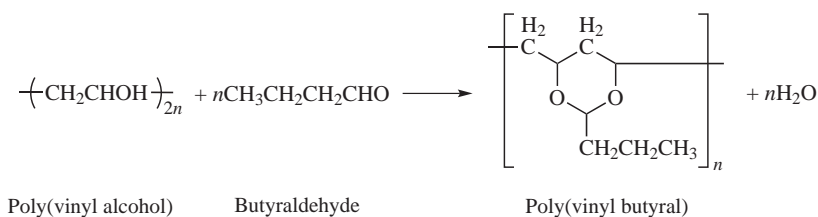
Although the liquid phase process never really worked, it is of interest because the water produced in the reaction leads to by-product acetaldehyde. This can be oxidized to acetic acid, which can be returned to the reactor. The system can be varied so that acetaldehyde is produced in just the right quantity to provide, on oxidation, the correct amount of acetic acid. In most two-for-one reactions (two products, in this instance acetaldehyde and vinyl acetate, from one set of equipment) the ratio of the products cannot be varied (cf. phenol–acetone production, Section 6.6) and accordingly a market must exist for the products in the ratio in which they are produced. Here the ratio may be varied by controlling the concentration of water. This same flexibility has been demonstrated in a relatively new process that produces both acetic acid and acetic anhydride (Section 12.5.2.3), and in a process for making ethylene glycol and dimethyl carbonate (Section 5.7.1).

The heterogeneous gas phase process is now generally used. The sodium acetate trickle is necessary because the acetate, essential to the catalyst's performance, migrates continuously. By-products include acetaldehyde, as might be expected, together with methyl and ethyl acetates. The conventional design for the heterogeneous gas phase vinyl acetate process employs a tubular fixed reactor. Ethylene conversion per pass is typically around 10% and selectivity to vinyl acetate is about 94–95%, based on ethylene. In 2001, BP commissioned a 250,000 metric ton/year fluidized bed plant in Hull (UK) using a novel palladium–gold catalyst. This is now operated by INEOS. It offers several advantages: improved mixing of catalyst, promoters, and feedstock; continuous removal of deactivated catalyst and addition of replacement catalyst; isothermal operation; lower capital investment; and the potential to scale-up to sizes not possible with tubular reactors.¹⁵

An uncommercialized process for preparing vinyl acetate from methanol is described in Section 12.5.2.7.

Vinyl acetate's major use is for conversion to poly(vinyl acetate), the basis of many adhesives and water-based emulsion paints (Fig. 5.10). Some poly(vinyl acetate) is converted to poly(vinyl alcohol) by saponification or more often by transesterification with methanol to give methyl acetate as a coproduct. Ethanol may also be used, giving ethyl acetate byproduct. Poly(vinyl alcohol) reacted with formaldehyde is used in Japan as the basis of Vinyon fibers, which found their most spectacular application in the manufacture of the durable Mao uniform in Communist China.

On reaction with butyraldehyde (Section 6.9), poly(vinyl alcohol) gives poly(vinyl butyral):



It forms the inner layer in safety glass, which is a sandwich of two sheets of glass held together by a layer of poly(vinyl butyral). The refractive index of poly(vinyl butyral) is the same as that of glass, hence its presence is unnoticeable, but its "stickiness" prevents the glass from shattering.

5.7 ETHYLENE OXIDE

The most important ethylene-based chemical that is not primarily a polymer precursor is ethylene oxide. It is made (Fig. 5.2h) by direct reaction of ethylene and oxygen over

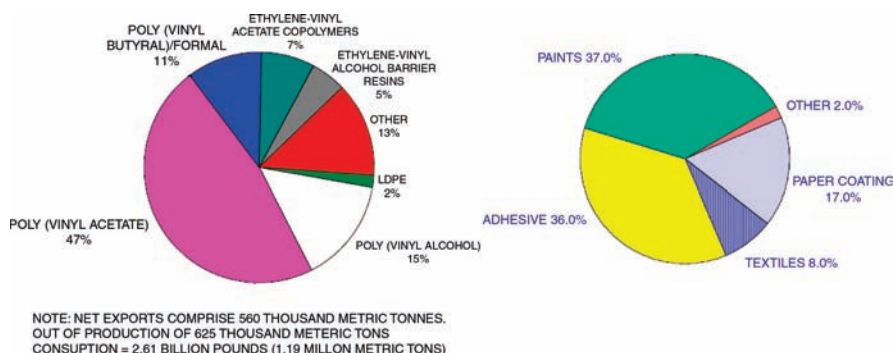
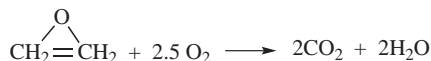
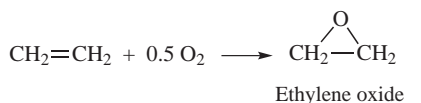


FIGURE 5.10 Vinyl acetate end-use pattern, United States, 2008.

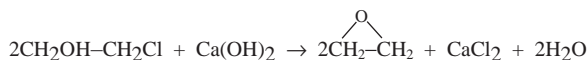
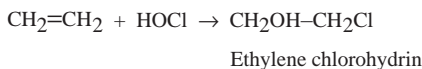
a silver catalyst (Section 18.1.1). The reaction is exothermic, and the simultaneous even more exothermic oxidation of both ethylene and ethylene oxide leads to the by-products, carbon dioxide and water.



Ethylene oxide technology provides an excellent example of yield improvement through incremental advances in catalyst technology. High selectivity is important because approximately 75% of the cost of ethylene oxide derives from the raw material, ethylene. Initially, selectivity with a silver catalyst supported on alumina was on the order of 65–70%. Because of improved catalysts, selectivities now average about 82% over the length of catalyst life and, at the start of a run, the very latest silver catalysts give over 90% selectivity. Shell Development, Union Carbide (now Dow Chemical), and Halcon/Scientific Design have numerous patents describing improved catalysts. One of Shell's patents discloses the addition of minute amounts of potassium, rubidium, or cesium ions to a silver catalyst to increase yields. Apparently the concentration of the added ions is critical.

The reaction is carried out at 15 bar and 250°C. A few parts per million of ethylene dichloride are frequently included in the reaction mixture to inhibit oxidation of ethylene to carbon dioxide and water. The ethylene dichloride decomposes to give chlorine atoms, which adsorb preferentially on the silver surface on the sites where oxygen would otherwise chemisorb to catalyze the combustion reaction.

The direct addition of oxygen to a double bond, discovered in the 1930s by Union Carbide, provides a striking example of the power of catalysis. The original process for ethylene oxide production, now obsolete, involved addition of hypochlorous acid to ethylene to give ethylene chlorohydrin, which with calcium hydroxide underwent a dehydrohalogenation to provide ethylene oxide and calcium chloride.



The process was wasteful of chlorine and, although yields were high, dilute solutions were necessary. The calcium chloride, whose weight was three times greater than that of the product, provided disposal problems. Also, since HOCl forms in an equilibrium reaction ($\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCl} + \text{HOCl}$) ethylene dichloride was a by-product as was chloroethyl ether, $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$.

In 2008, about half of U.S. ethylene oxide was hydrolyzed to ethylene glycol (Section 5.7.1). Other major uses include reaction with alkylphenols, fatty alcohols (Section 15.8), fatty amides and amines (Section 15.4), and anhydrosorbitol to yield nonionic surfactants (Fig. 5.11). The ethoxylated alkylphenols are the most important. Hydroxyl-terminated polymers of ethylene oxide and propylene oxide are useful as isocyanate coreactants for urethanes. Ethylene oxide reacts with ammonia to provide aminoethyl alcohols (Section 5.11.6.4) and may be converted to poly(ethylene glycols) (Section 5.11.6.1).

West European ethylene oxide end uses reflect lower use of antifreeze and production of polyester fibers, and greater production of surfactants. The polyester fiber business has been built up in Asia-Pacific, and 81% of their ethylene oxide production goes into ethylene glycol.

Ethylene oxide reacts with starch and cellulose to provide hydroxyethyl derivatives (Sections 16.3 and 16.4). The former is a more readily dispersible form of starch, which finds application in both food formulation and paper manufacture. The latter is a thickener for water-based paints and a protective colloid for water dispersions.

5.7.1 Ethylene Glycol

Ethylene glycol is prepared either by the acid catalyzed or more often by the uncatalyzed hydration of ethylene oxide (Fig. 5.2h). A huge excess of water is used

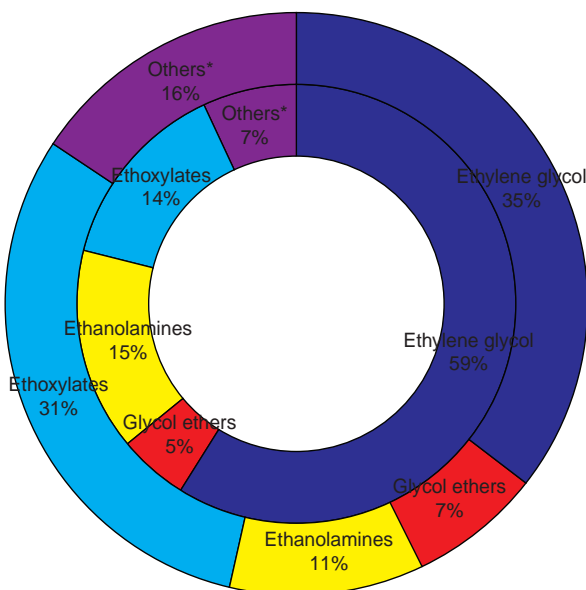
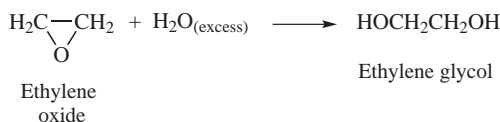


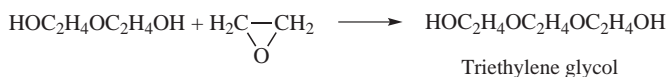
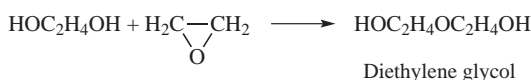
FIGURE 5.11 Ethylene oxide end uses, 2009. Inner ring: United States (3.7 million metric tons). Outer ring: Western Europe (2.8 million metric tons). * Mainly diethylene and triethylene glycols. (Source: Nexant Inc.)

(18–24 mol of water per mol of ethylene oxide) to prevent the formation of di-, tri-, and higher ethylene glycols. Even with high water-to-ethylene oxide ratios, mono-, di-, and triglycols are obtained in a weight ratio of about 91:8.6:0.4.

Desired reaction

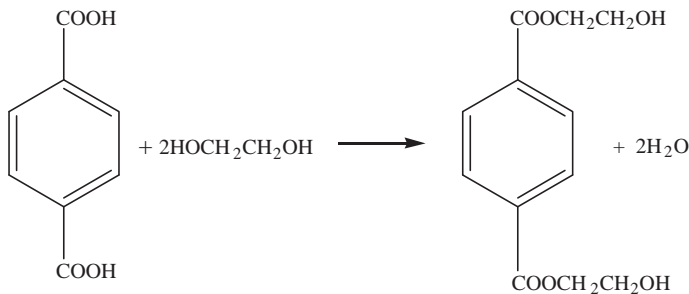


Side reactions

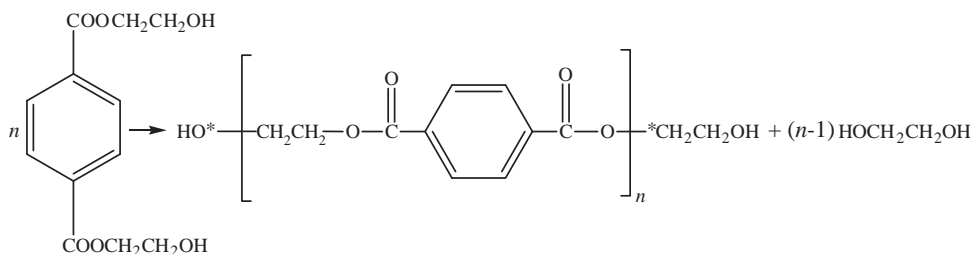


The reaction of ethylene oxide with glycols may form oligomers of ethylene oxide, and they may be prepared in this way “on purpose,” if needed, by the side reactions shown.

Purification of the ethylene glycol is complex, requiring repeated fractional distillations to remove the water and to separate the glycol from its oligomers. High purity is necessary for the preparation of polyester resins, one of ethylene glycol’s two major uses. About 68% of ethylene glycol production is reacted with purified terephthalic acid or sometimes with dimethyl terephthalate to produce poly(ethylene terephthalate) (Sections 11.3.3 and 17.1). The availability of high purity terephthalic acid has made the dimethyl terephthalate route obsolescent. The production of water rather than methanol as the by-product is an advantage. The first stage of the process starting with terephthalic acid is an esterification reaction:



Terephthalic acid or dimethyl terephthalate provide the same intermediate that undergoes a polycondensation to provide the polymer.



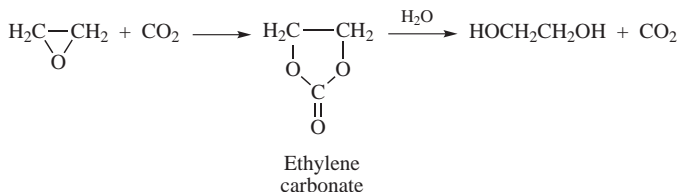
The conventional process consists of two discrete plant sections: a melt phase reaction section and solid-state polymerization section. The progress of the reaction is measured by the intrinsic viscosity (IV), which is an indirect measure of the chain length or molecular weight of the polyester chains. The IV of the bis dihydroxyethyl terephthalate prepolymer is about 0.25. The melt phase reaction gives a lower intrinsic viscosity product (IV = 0.6–0.65) that is suitable for textile applications but not for bottle grade and other high molecular weight applications. In the solid-state polymerization section, the lower molecular weight polymer is then further polymerized to bottle grade material (IV = 0.72–0.85).¹⁶

The lower intrinsic viscosity polymer may be spun into textile fibers; Dacron or Terylene are well-known brand names, but the polyester industry as a whole is depressed in developed countries and has migrated largely to Asia-Pacific. This is illustrated by the ethylene glycol consumption figures for 2009 as raw material for polyester. The United States consumed 12 million metric tons, Western Europe 1.02 million metric tons, and Asia-Pacific an astonishing 12 million metric tons, most of it imported by China.

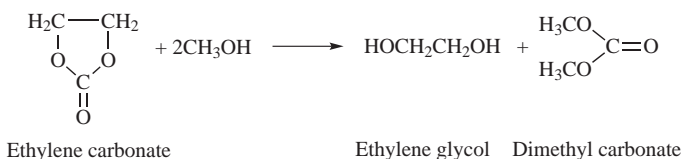
It can also be made into strong biaxially oriented films known as “Mylar.” This may be coated with magnetic material and used for magnetic tape, or vacuum-coated with metal, usually aluminum, to give a survival blanket. In the 1980s, high molecular weight poly(ethylene terephthalate) found an important application as a plastic for the fabrication of soft-drink bottles which grew rapidly and has only recently slowed (Section 11.3.3).

Ethylene glycol's other major use, a nonpolymer one, is as antifreeze in automobile radiators. In 2009 the United States used about 34% of its ethylene glycol for antifreeze; in Western Europe the figure was about 19% and in Asia-Pacific practically nil. The market is growing only slowly because sealed radiator formulations last longer. Of the 18 million metric tons global ethylene glycol market, 55% goes into fibers, 4% into film, 26% into bottle grade poly(ethylene terephthalate), 9% into antifreeze, and 7% into other industrial applications. Di- and triethylene glycol are described in Section 5.11.6.1.

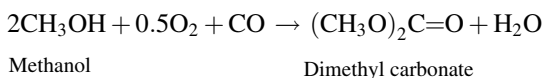
As noted above, the drawback of ethylene oxide hydrolysis is that, even with a large excess of water, about 9% of diethylene glycol and 1% of triethylene glycol are formed. A process for converting ethylene oxide to ethylene glycol with higher selectivity is described in Union Carbide (now Dow) and Texaco (now Huntsman) patents.¹⁷ It involves the reaction of ethylene oxide with carbon dioxide at 190°C and 13 bar to give ethylene carbonate (Section 5.11.6.3), which in turn reacts with water at the same pressure but at 170°C to give ethylene glycol and carbon dioxide. The first step is catalyzed by tetraethylammonium bromide and potassium iodide.



The process eliminates large excesses of water as well as the possibility for the formation of higher ethylene glycols. Union Carbide started to commercialize this process in a Canadian ethylene oxide/ethylene glycol plant. The winters in Canada are so cold, however, that the ethylene carbonate froze and plugged the process lines, so that the approach had to be abandoned. Shell, however, developed a so-called OMEGA process, which has similar chemistry. They opened a 400,000 metric tons per year plant in 2008, which gave less than 1% by-products. Shell plans a 750,000 metric tons per year plant near Singapore. A related but as yet uncommercialized approach is to react the ethylene carbonate with methanol to give a mixture of ethylene glycol and dimethyl carbonate, which can be separated by distillation.



Dimethyl carbonate was originally prepared from methanol and the highly toxic phosphene. The above route eliminates the hazard as does another route involving the oxidative carbonylation of methanol.



The reaction of carbon dioxide with diepoxides leads to carbonate polymers, which have not been commercialized but which are of interest because of their biodegradability. The use of dimethyl carbonate in a nonphosgene route to polycarbonates is described in Section 9.1.2.2.

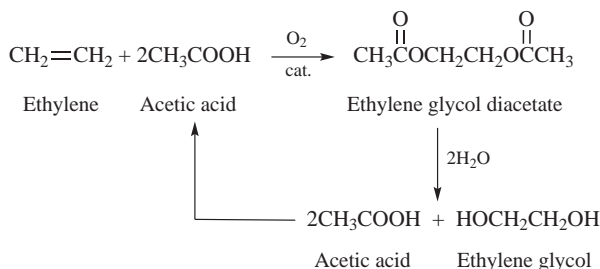
Still another means for reducing oligomer formation is described in a Carbide patent. The ethylene oxide hydrolysis is carried out with a vanadate or molybdate catalyst attached to an ion exchange resin.¹⁸ Only 2.5 mol of water is used per mole of ethylene oxide. One hundred percent selectivity to ethylene glycol at 100% conversion is claimed. The route has not been commercialized presumably because of the difficulty of removing traces of catalyst from the final product.

5.7.2 Proposed Non-Ethylene Oxide Processes for Ethylene Glycol Production

Even with improved catalysts, yields of ethylene oxide from ethylene epoxidation are on average only about 82%. Hence other processes for ethylene glycol are sought.

If an economic one were to be found, the market for ethylene oxide would be cut by 35% in Europe and 59% in the United States.

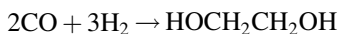
In one proposed reaction ethylene, acetic acid, and oxygen combine to give ethylene glycol diacetate. These are the reactants that give vinyl acetate in the Wacker process, but the proportion of acetic acid is greater, and a different catalyst, tellurium oxide with an alkyl halide, is used. Two ethylenic hydrogen atoms instead of one are substituted. The diacetate can be hydrolyzed to ethylene glycol and the acetic acid recycled so that the overall reaction involves only ethylene, air, and water.



A 360,000 metric ton per year plant was built in the late 1970s but corrosion problems not unlike those associated with the original liquid phase vinyl acetate plant (Section 5.6) proved its downfall.

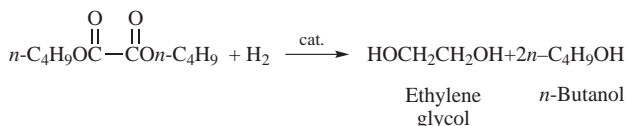
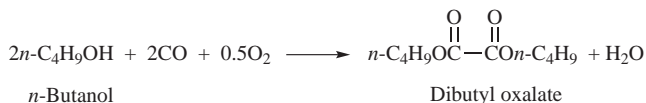
Although corrosion-resistant materials could undoubtedly be found to withstand the chemistry of this process, there has been no attempt to revive it, but Mitsubishi is using the same chemistry successfully for the manufacture of 1,4-butanediol (Section 7.1) from butadiene. Because of the greater reactivity of the conjugated double bond system, a catalyst comprising palladium and tellurium without halide can be used, so that the environment is less corrosive.

Union Carbide (now part of Dow) pioneered a process for ethylene glycol based on the direct combination of carbon monoxide and hydrogen:

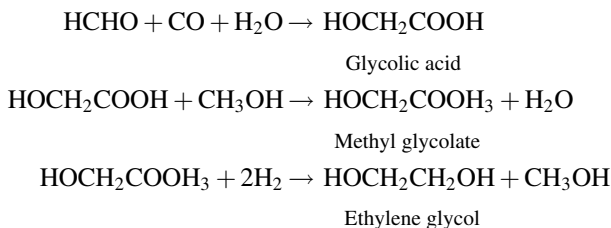


Union Carbide investigated many catalysts, including rhodium carbonyl cluster catalysts, which require temperatures of 240°C and pressures of 1000–3000 bar. In other studies a ruthenium carbonyl complex and an organosilicon compound such as trimethylethoxysilane were used at 400°C and 1000 bar. Selectivity to ethylene glycol is 60–65% and methanol is the major coproduct. Methyl formate, other esters, 1,2-propanediol, glycerol, and water are also formed.

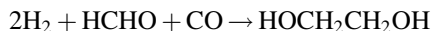
This poor selectivity led Carbide to join forces with Ube Industries in Japan to develop a process based on the hydrogenolysis of oxalate esters, compounds that Ube had investigated extensively as described in Section 12.6.1. Selectivity is usually improved when reactions are carried out stepwise. Thus in the first step di-*n*-butyl oxalate results, which on hydrogenolysis yields ethylene glycol and butanol for recycling.



The second step is similar to one used by DuPont until 1968 in which formaldehyde was carbonylated in the presence of water to give glycolic acid at 200°C and 700 bar. The esterification of the acid with methanol provided methyl glycolate, which, on hydrogenolysis, yielded ethylene glycol and methanol for recycling,

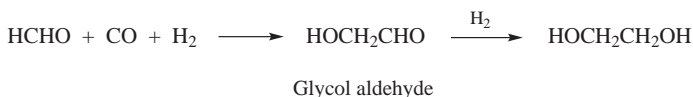


The carbonylation takes place at 200°C and 70–100 bar at high selectivity, as does the esterification reaction. The hydrogenolysis occurs at 200°C and 30 bar with an appropriate catalyst. The released methanol is recycled so that the overall reaction is

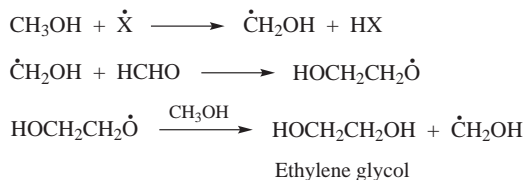


An improvement in the process involves the use of HF in the carbonylation step. Coupled with the development of more active catalysts for the hydrogenolysis (Section 12.3), this could make the DuPont process attractive if coal-based synthesis gas became a major feedstock.

A Monsanto process for ethylene glycol is based on the hydroformylation of formaldehyde in the presence of a homogeneous rhodium catalyst. The ligand is tri(*p*-trifluoromethylphenyl)phosphine together with triethylamine. Glycol aldehyde results, which on hydrogenation yields ethylene glycol.



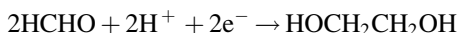
A free radical-induced chain reaction between methanol and formaldehyde provides the basis for an interesting process in which free radicals from di-*tert*-butyl peroxide convert methanol to a hydroxymethyl radical. This radical attacks formaldehyde to provide an ethylene glycol radical, which attacks another molecule of methanol to provide ethylene glycol and a hydroxymethyl radical for further propagation.



Unfortunately, the chains in the process are too short, and many of the hydroxymethyl radicals couple to provide ethylene glycol and terminate the chain reaction. Thus consumption of the peroxide initiator is unacceptably high.



Another approach involves the electrohydrodimerization of formaldehyde. The problem, as in all electrochemical reactions, is to obtain adequate current efficiencies.



Improved catalysts for ethylene oxide production and the difficulties involved in the direct routes have prevented the commercialization of any of the routes to ethylene glycol that do not go via ethylene oxide, despite the apparent possibility of higher overall yields based on ethylene and the large growth in glycol demand stemming from the explosion of poly(ethylene terephthalate) consumption.

5.8 STYRENE

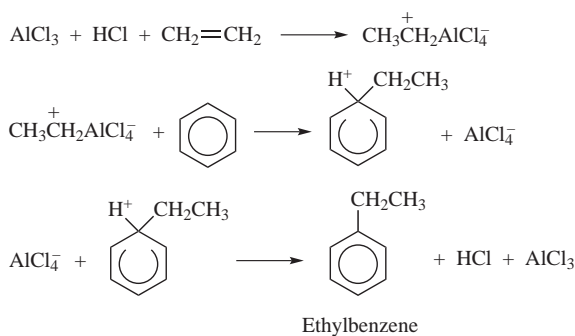
After polyethylene and poly(vinyl chloride), the third large tonnage polymer to be made from ethylene is polystyrene. Its monomer, styrene, was used initially not in polystyrene but in a copolymer with butadiene that served as a substitute for natural rubber. Germany had started commercial production of Buna S rubber in 1938 and during World War II was totally dependent on it. With the capture by Japan of the rubber producing areas of Southeast Asia, the United States too was forced into a crash program for synthetic rubber development. The Buna S-type (GR-S) rubber was the result of an admirable coordinated effort between many academic, industrial, and government laboratories. If either side in the war had lacked synthetic rubber, its war effort might have collapsed.

Synthetic rubbers now account for about 59.4% of world consumption, excluding thermoplastic rubbers, which account for 5.4%, leaving 35.2% for natural rubber. Natural rubber styrene-butadiene (SBR) rubber, the descendant of Buna S and GR-S, is the preferred material for automobile tires together with lesser amounts of polybutadiene rubber, butyl rubber, and natural rubber (Section 7.1) and accounts for rather over half of world synthetic rubber production. Natural rubber has gained market share since the 1970s, first from the replacement of cross ply tires by radial ply,

and second because its price has remained more or less stable in the face of higher petroleum prices.¹⁹

Styrene is widely used in copolymers as well as in homopolymers and rubber-modified styrene polymers. It provides an example of a “classical” reaction for ethylene. The major process for styrene manufacture involves a Friedel–Crafts reaction between benzene and ethylene to form ethylbenzene. Some ethylbenzene is also produced during catalytic reforming (Section 4.8) and can be removed from the C₈ fraction by so-called superfractionation. Dehydrogenation to styrene in the presence of steam and a catalyst provides styrene and hydrogen (Fig. 5.2i). An alternate process for styrene, to be described later (Section 6.8), gives propylene oxide as a coproduct. It is used commercially by Lyondell, Repsol, and Ellba, a joint venture between Shell and BASF, that subsequently has become LyondellBasell. It is the main competitor for the ethylbenzene dehydrogenation route.

The Friedel–Crafts alkylation was initially carried out at 85–95°C at atmospheric pressure in the liquid phase with aluminum chloride and a small amount of HCl. In one process, boron trifluoride is used. The mechanism is well-established:



Yields are high, but small amounts of di- and polyethylbenzenes result because the alkylaryl complex is more reactive than the hydrogen aryl complex and can continue to add ethyl groups. The di- and polyethylbenzenes are recycled and transalkylated with excess benzene to give ethylbenzene. The aluminum chloride catalyst originally used is corrosive and hard to dispose of. An improvement was the development of zeolite ZSM-5 as a catalyst in a continuous vapor phase reaction that can operate at a temperature of 400°C at 18 bar. The higher temperature makes heat recovery easier, and the product is obtained in 99.5% selectivity with 98% ethylene conversion. In 2006, UOP offered a more selective catalyst, UZM-8, developed by their zeolite screening program.

The dehydrogenation is endothermic and requires a high temperature (550–600°C) and low pressure. As in steam cracking (Section 4.5.1), superheated steam is added to inhibit coking and reduce the partial pressure of the reactants. The catalyst is highly selective. Its major component, present usually to the extent of more than 50%, comprises the oxides of iron, cobalt, manganese, chromium, or zirconium. If iron oxide is used, another oxide is added as a stabilizer to keep the iron in the ferric state. Alkaline metal oxides, particularly potassium and rubidium oxides, are effective.

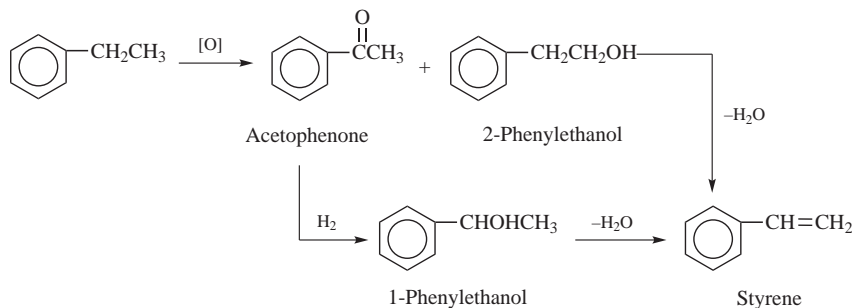
A third ingredient is a carbon formation inhibitor, which may also be the oxide of potassium or rubidium. An oxide of copper, silver, cadmium, thorium, or vanadium is added as a secondary promoter to increase the effectiveness of the primary active ingredient. A “cement” such as calcium aluminate aids pellet formation. Organic substances such as methylcellulose may be included to introduce porosity when they burn off during the calcining of the catalyst.

The oxidative dehydrogenation of styrene was never considered practical because both ethylbenzene and styrene are oxygen-sensitive. In the mid-1980s UOP described a new catalyst, to be used in combination with present catalysts. It preferentially oxidizes to water the hydrogen produced from the ethylbenzene in a separate step, thus not affecting the other components of the reaction mixture. It comprises platinum, tin, and lithium on alumina. Since water formation is exothermic, the heat generated reduces the superheated steam input necessary in the current process. This development was commercialized in the late 1990s.

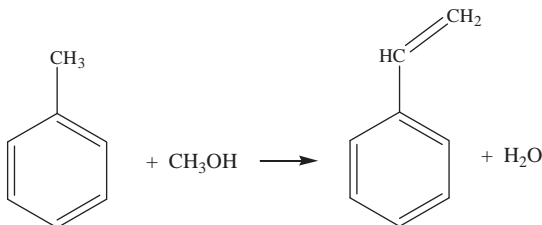
Dow has proposed a route to styrene by oxydehydrogenation of 4-vinylcyclohexene prepared by butadiene dimerization²⁰ (Section 7.1.6.2). The dimerization is performed in the gas phase at 100°C and 25 bar over a proprietary catalyst consisting of copper-loaded Y-zeolite. The second step is oxydehydrogenation of vinylcyclohexene to styrene. This reaction is catalyzed by mixed metallic oxides in the vapor phase at about 400°C and 2.4 bar.

A variant of this process, developed by DSM, hydrogenates the vinylcyclohexene to ethylbenzene. The dehydrogenation can then be carried out in a conventional plant. The DSM process employs liquid phase butadiene dimerization to 4-vinylcyclohexene catalyzed by iron dinitrosyl chloride/zinc complex $[\text{Fe}(\text{NO})_2\text{Cl}/\text{Zn}]$, while the dehydrogenation to ethylbenzene is catalyzed by palladium on magnesium oxide. Final conversion of ethylbenzene to styrene can be carried out with conventional dehydrogenation catalysts. Other proposed routes are the conversion of toluene to stilbene followed by metathesis with ethylene (Section 10.4), and the ZSM-5-catalyzed alkylation of toluene with methanol. The literature contains references to the production of styrene directly from benzene and ethylene in the presence of oxidants for the liberated hydrogen. Apparently, none of these routes can compete economically with the conventional route, and we have not noticed plans for commercialization.

An obsolete process for styrene production involved oxidation of ethylbenzene to acetophenone and 2-phenylethanol followed by hydrogenation of the acetophenone to 1-phenylethanol, which dehydrates easily to styrene.



In spite of the above variants, the dominant technology of styrene manufacture has remained essentially unchanged for 70 years. All the same, in 2010, costs per metric ton of methanol and toluene were, respectively, \$350 and \$650 compared with benzene and ethylene at \$940 and \$1100. This provides an incentive for the development of a route to styrene by side-chain alkylation of toluene with methanol, and such a process has been investigated for over 30 years. Low product yields have prevented it from being used commercially.



A small company, Exelus, claims to have developed a catalyst providing yields of over 80%.²¹ The route is single step and takes place at 400°C, much less than the corresponding temperatures in the traditional process. It offers an 80% reduction in energy requirement and avoids the need for difficult and expensive dehydrogenation. *para*-Methylstyrene was at one time proposed as an alternative monomer to styrene. It is made by the ZSM-5-catalyzed alkylation of toluene with ethylene. This zeolite catalyst is *para*-orienting providing high selectivity to *para*-methylethylbenzene. Dehydrogenation of the ethyl group provides *para*-methylstyrene. Since toluene is cheaper than benzene, *para*-methylstyrene should enjoy an economic advantage. In fact, the initial lower scale of production and escalating toluene prices in the mid- and late 1980s eliminated this advantage and the product was not commercialized.

Styrene's major use is for the manufacture of polystyrene, almost half of which is used for disposables such as packaging and plastic cups and cutlery. The remainder goes into radio and TV cabinets, toys, door liners and trays for refrigerators, housings for small appliances such as clocks, housewares, furniture components, and in construction for window moldings, window shutters, and pipes. The longer lasting applications such as radio cabinets require so-called high impact styrene (HIPS), made by polymerizing styrene in the presence of polybutadiene elastomer. A large use is for audio and video cassettes and for support materials for magnetic tapes.

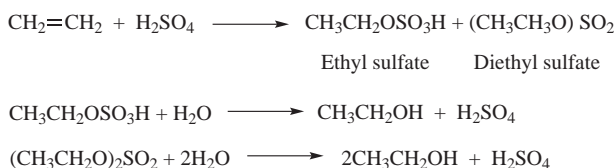
The second largest use for styrene is for elastomers including styrene–butadiene rubbers and latexes. An important application is in so-called thermoplastic rubbers, typical of which is a block polymer of polystyrene–polybutadiene–polystyrene (Section 7.1).

The third largest use is in styrene copolymers, of which the most important is acrylonitrile–butadiene–styrene (ABS), an engineering polymer widely used for computer and calculator cases, telephones, and related applications. The acrylonitrile provides strength, the butadiene flexibility and impact resistance, and the styrene gloss and hardness. Styrene is also found in styrene–acrylonitrile (SAN) and styrene–maleic anhydride copolymers. The latter is glass-like and is useful for cosmetic bottles with decorative shapes.

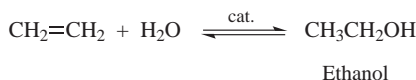
The fourth most important use for styrene is as a reactive solvent for unsaturated polyesters, which, after curing, become thermoset copolymers of styrene and the polyester (Section 11.1.2).

5.9 ETHANOL

Ethanol was first produced from ethylene, instead of by fermentation, in 1930. Ethylene was reacted with sulfuric acid to provide ethyl sulfate and diethyl sulfate, both of which were hydrolyzed to ethanol. Sulfuric acid was recycled. Diethyl ether is a by-product and indeed the reaction can be run selectively to provide it (Section 5.11.10).



The above process was replaced by direct hydration in which water is added to ethylene over a phosphoric acid catalyst on silica or celite.



Selectivity to ethanol is on the order of 92–98%. There is a problem, however, in that high temperatures are required to give acceptable rates of reaction but, as in the classic Haber process (Section 12.5.1), the higher temperatures favor the ethylene/water side of the equilibrium. Under optimum conditions, conversion per pass may be as low as 4%, although 20% has been reported. This means that large amounts of ethylene must be recycled.

Typical reaction conditions for the direct hydration are 300°C and 69 bar. The crude ethanol is purified by distillation to produce an azeotrope with water containing 95.6 volume percent ethanol. Absolute or 100% ethanol is usually prepared by azeotropic distillation. Benzene is added and the mixture distilled. The ternary azeotrope that distills carries the benzene and water with it, leaving anhydrous alcohol as the bottom product. Another method uses countercurrent extraction with glycerol or ethylene glycol. The added component hydrogen bonds to the water and allows anhydrous alcohol to be obtained from the top of the column. Less energy-intensive methods for obtaining anhydrous ethanol provide an active area of research. Membrane technology has apparently held promise for at least two decades, but its development is slow.

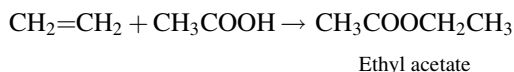
Until about 1950, ethylene was expensive and was obtained from fermentation ethanol by dehydration – the reverse of the above processes. With the advent of cheap ethylene from steam cracking, the petrochemical route to ethanol became more economical than fermentation. By the early 1970s, scarcely any industrial ethanol was

made by fermentation in the United States, although there was a legal requirement in most countries that potable ethanol be made in the traditional way.

In the United States in the 1980s, this trend was reversed when government subsidies were introduced to facilitate the production of ethanol by fermentation of corn starch. The product went into automotive fuel known as gasohol. Fermentation ethanol is not economical without subsidies. Whether it provides a positive energy balance considering the energy required to grow the corn, isolate the starch from it, and distill the resulting ethanol was controversial, but there is modest agreement that, given modern farming methods, there is a positive balance of uncertain magnitude. Fermentation alcohol is discussed in Chapter 16 and Section 4.15.1.

The development of gasohol has motivated the development of other routes to ethanol, the most important of which is methanol homologation, as yet uncommercialized (Section 12.6.1).

Ethanol was once the basis for acetaldehyde and acetic acid production (Section 5.5) and this still may be practiced to a small extent in India and Brazil. In these countries ethylene was also prepared by the dehydration of ethanol until the mid-1980s. With the advent of huge productive facilities for fermentation ethanol, new plants have been built in Brazil for its dehydration to ethylene. In addition to gasohol, ethanol has humble uses for ethyl ester formation. Ethyl acetate is made by esterification of acetic acid with ethanol, from acetaldehyde (Section 5.5), or by the direct addition of ethylene to acetic acid. BP started a 220,000 metric ton/year plant in 2001 to operate the last of these processes, known as AVADA. Ethylene and acetic acid react in the presence of a heteropolyacid catalyst to give ethyl acetate at a claimed high selectivity and 99.97% purity.²² This is the world's largest ethyl acetate plant and is motivated by its increasing use as a more "acceptable" solvent than hydrocarbons.



In some countries, where ethanol is expensive or there is surplus acetaldehyde capacity, ethyl acetate is made by a Tishchenko reaction (Section 5.11.3). Sasol in South Africa built a 50,000 metric tons/year plant in the 2000s said to be based solely on ethanol but it is not clear if it is first oxidized to acetaldehyde.²³ Ethanol is a solvent for surface coatings, cleaning preparations, and cosmetics. Industrial ethanol is aerobically fermented by acetobacter bacteria to white vinegar (dilute acetic acid) of the type used for pickling. Gourmet vinegars – wine vinegar, cider vinegar, and so on, made by fermentation of alcoholic beverages – are also available.

5.10 MAJOR CHEMICALS FROM ETHYLENE – A SUMMARY

Sections 5.1–5.8 have described the "major" chemicals from ethylene, that is, chemicals that are produced in the United States at a level of more than about half

a million metric tons per year. These chemicals and their production volumes for 1990, 2000, and 2009 are shown in Table 5.3 together with growth rates over this period. The sixth column gives the quantity of ethylene required to give the product, if it is made directly from ethylene. Thus figures for ethylbenzene and ethylene dichloride are given and not for styrene and vinyl chloride, which are made from them. Only one polymer family, polyethylenes, is included in the table since these are made directly from ethylene. Styrene, vinyl chloride, ethylene glycol, and vinyl acetate are all important monomers for polymers. Indeed this is the most important use for all the chemicals except ethanol and ethylene oxide. The latter is mainly converted to ethylene glycol, for use in polymers and antifreeze, but the polymer application is now dominant.

Four chemicals – acetic acid, acetic anhydride, acetaldehyde, and ethanol – lost volume precipitously between 1977 and 2009 insofar as they were based on ethylene. Acetic acid, acetic anhydride, and acetaldehyde were displaced by processes for acetic acid production, especially methanol carbonylation (Section 12.5.2.2), which did not involve ethylene. Acetic acid from ethylene-based acetaldehyde was formerly acetaldehyde's most important use. Acetic anhydride may be made from acetic acid via intermediate production of ketene or by a carbonylation route of methyl acetate. Accordingly it too is no longer ethylene-based.

Ethanol was formerly a raw material for acetic acid too, because it was oxidized to acetaldehyde prior to the advent of the Wacker process (Section 5.5), but that application disappeared in the 1970s. However, ethanol production in the United States has plummeted more recently (Table 2.3) because of imports from Saudi Arabia.

A relative newcomer to the list of major chemicals is α -olefins, some of which are converted to fatty alcohols (Section 5.3). Fatty alcohols as ethoxylates or sulfates are increasingly used in surfactants for detergents because of their greater biodegradability. α -Olefins are comonomers in linear low density and high density polyethylene production. 1-Decene finds a growing use because its trimer is a synthetic lubricant. C_{12} – C_{18} α -olefins are converted to C_{13} – C_{19} alcohols by hydroformylation (Section 6.8) for use in surfactants and C_6 – C_8 α -olefins yield C_7 – C_9 alcohols for plasticizers (Section 11.1.1).

Much of the growth in ethylene consumption came from the polyethylenes, which continue to find new applications. LDPE usage is declining as it is being replaced by linear low density polyethylene (LLDPE). A market for LDPE will continue because in some applications it is used in combination with LLDPE to give easier molding and extrusion and because it is essential for extrusion coating of paper board for milk and juice cartons.

The sixth column of Table 5.3 shows the amount of ethylene going into each of the end uses. The requirements of these major end uses account for 90% of ethylene consumption even on the basis of the assumed 100% yields. That leaves about 10% to go into the myriad lesser volume chemicals, which will be discussed in the remainder of this chapter.

TABLE 5.3 Global Ethylene Production and Consumption Patterns (1990, 2000, 2009)

Polymer or Chemical	1990	2000	2009	Average Annual % Increase 2000–2009	Ethylene Consumption, 2009 ^a	United States End-Use Pattern	Western European End-Use Pattern	Asia-Pacific End-Use Pattern
	(thousand metric tons)							
Ethylene	54,518	89,499	114,353	2.8	114,353			
Polyethylenes	30,292	51,138	70,152	3.6				
LDPE	14,078	16,502	18,594	1.3	18,502	13.4%	22.9%	14.1%
LLDPE	4,472	12,308	20,176	5.6	19,072	14.8%	12.9%	16.2%
HDPE	11,742	22,328	31,382	3.9	31,412	29.3%	22.2%	27.1%
Ethylene dichloride	28,141	36,002	38,795	0.8	12,970	15.6%	14.0%	11.6%
Styrene	13,527	20,748	24,549	1.9	7,098	5.6%	6.6%	8.7%
Ethylene oxide	7,248	13,830	20,849	4.7	15,943	10.5%	10.2%	15.6%
Vinyl acetate	1,955	2,977	3,927	3.1	1,394	1.9%	1.2%	1.7%
Ethanol							0.8%	
Acetaldehyde							0.6%	
α-Olefins						5.7%	2.6%	
Other					7962	3.2%	6.1%	5.0%

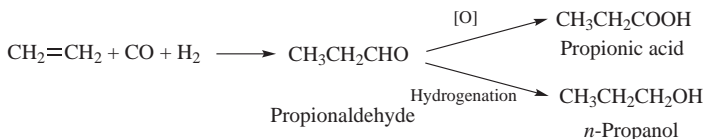
^aThis figure is the ethylene required to give 2009 production. Yields are assumed to be 100%, except for ethylene oxide, where 80% is assumed.

5.11 LESSER VOLUME CHEMICALS FROM ETHYLENE

This section deals with chemicals from ethylene that are produced in volumes of less than half a million metric tons per year in the United States. The chemicals are listed in Table 5.1.

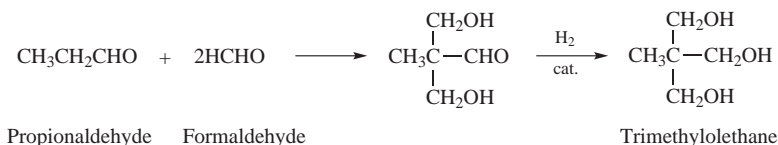
5.11.1 Hydroformylation – Propionaldehyde, Propionic Acid, and *n*-Propanol

The oxo or hydroformylation reaction with ethylene produces propionaldehyde, which in turn can be oxidized to propionic acid or reduced to *n*-propanol.



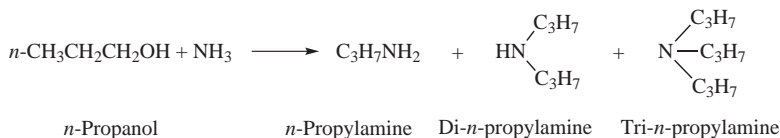
Hydroformylation, which is discussed in Section 6.8, was carried out initially with a dicobalt octacarbonyl, $(\text{Co})_2(\text{CO})_8$, catalyst at temperatures of about 150°C and 250–300 bar. A breakthrough was the discovery that rhodium chloride with ligands such as triphenylphosphine allowed the reaction to take place at temperatures of around 100°C and 10–25 bar. Hydrogenation of the aldehyde to the alcohol takes place with a nickel catalyst at 2–3 bar at about 115°C in the gas phase. In the liquid phase, higher pressures are required.

Propionaldehyde reacts with formaldehyde to provide trimethylolethane.



The formaldehyde condenses with the two active hydrogens to give a dimethyloaldehyde. The aldehyde group may then be reduced in situ by another mole of formaldehyde, which is itself oxidized to formic acid. Alternatively, the dimethyloaldehyde may be isolated and reduced catalytically. The same chemistry is used to synthesize pentaerythritol (Section 5.11.3) and trimethylolpropane (Section 12.5.2.1). Trimethylolethane is used for alkyl resins and urethanes (Section 9.3.1).

n-Propanol reacts with ammonia to form mono-, di- and tripropylamines:

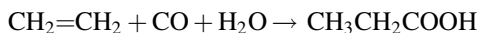


One of *n*-propanol's important uses is as a solvent, particularly for flexographic inks used with natural rubber rolls that would be attacked by more powerful solvents.

Natural rubber rolls are necessary because printing on plastic film requires high flexibility and low hysteresis losses. *n*-Propanol also finds small use in the production of propyl esters such as propyl acetate.

Propionic acid may be made by the oxidation of propionaldehyde. The liquid phase reaction is catalyzed by a cobalt salt at 100°C and 6–7 bar.

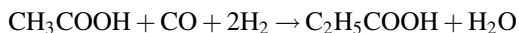
An alternative process involves the carbonylation of ethylene by a so-called Reppe reaction, which is carried out with a nickel carbonyl catalyst in the liquid phase at 200–250 bar and 300°C. Nickel carbonyl is poisonous and in this reaction it is formed *in situ*.



Propionic acid

A low pressure process for carbonylation of ethylene in the presence of water, which has not been commercialized, makes use of a nickel–molybdenum carbonyl catalyst with iodide and phosphoric acid promoters at about 200°C and 10–30 bar.

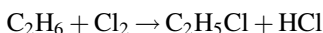
The route to acetic acid by oxidation of naphtha (Section 13.2.1) gives propionic acid as a by-product. In the UK, such a plant was kept in operation until the 1990s because of the value of the by-products. A proposed propionic acid synthesis involves the homologation of acetic acid with CO and H₂ at 220°C and 270 bar. Butyric and valeric acids form as minor coproducts. The reaction is homogeneous and is catalyzed by ruthenium or rhodium with ligands such as acetylacetonate, with an iodide promoter or cocatalyst.



The major use of propionic acid is as a feed and grain preservative. An important use, particularly for the calcium or sodium salts, is as a food preservative especially in baked goods. A minor use is for the preparation of cellulose propionate via propionic anhydride.

5.11.2 Ethyl Halides

Ethyl chloride and ethyl bromide can be made by the addition of the corresponding hydrogen halides to ethylene. The reaction between ethylene and hydrogen chloride takes place either in the liquid or the gas phase at moderate temperatures and pressures with halide catalysts such as AlCl₃. A second process involves the chlorination of ethane, which, unlike methane (Section 10.2), gives 80% ethyl chloride before the dichloro compound starts to form. The chlorination of ethane generates ethyl chloride and hydrogen chloride, which can then be added to ethylene to provide more ethyl chloride in an integrated process.



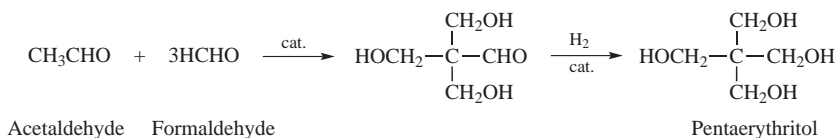
The chlorination reaction takes place at 400°C. Since chlorine will not add to an olefin (Section 6.11.1) at this high temperature, the ethylene and ethane may be in the same reaction mixture, the chlorination of the ethane taking place in the presence of the essentially inert ethylene.

A route to ethyl chloride from ethanol and hydrogen chloride is obsolete because ethanol is more expensive than either ethane or ethylene.

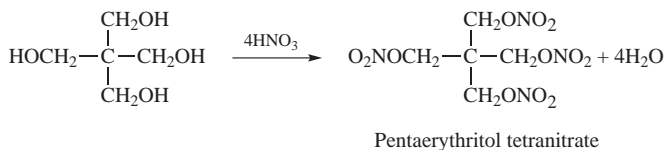
Ethyl chloride consumption in the United States in 1974 was 300,000 metric tons. By 1991 this had dropped by 80% and has now virtually disappeared. Its major use was in the manufacture of lead tetraethyl, an octane improver for gasoline. The tetraethyl was combined with lead tetramethyl to control volatility. Both of these were almost completely phased out from the United States by 1991. Ethyl chloride is still used to etherify cellulose to ethyl cellulose. Small quantities are consumed as solvents, refrigerants, and topical anesthetics. It is also a recreational inhaled drug, known as “duster.” Ethyl bromide is a low volume specialty chemical which, like its chlorine analog, can be made either by the addition of HBr to ethylene or by the bromination of ethane.

5.11.3 Acetaldehyde Chemistry

Acetaldehyde has been discussed previously (Section 5.5) as a derivative of ethylene whose consumption has declined because its major uses have disappeared. Nonetheless, in 2003, a million metric tons was produced globally. There are many lower volume chemicals still requiring acetaldehyde. Acetaldehyde with formaldehyde in the presence of alkali yields pentaerythritol:

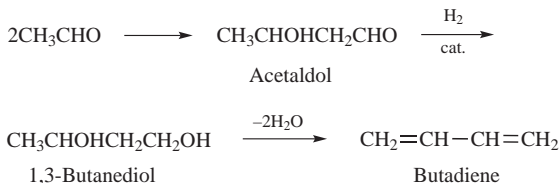


In pentaerythritol, as in trimethylolethane formation, the aldehyde group of the trimethylolacetaldehyde may be reduced by a mole of formaldehyde, which oxidizes to a mole of formic acid in a crossed Cannizzaro reaction. Calcium hydroxide is frequently used as a catalyst. Alternatively, the aldehyde may be reduced catalytically. Sixty percent goes into alkyd resins, 16% into neopolyol esters for lubricants, and 11% into rosin and tall oil esters. The tetranitrate is an explosive and is also a vasodilator for the treatment of angina pectoris, as is the more widely used glyceryl trinitrate, but it consumes only 4% of production.

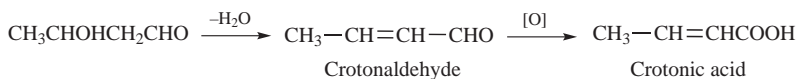


Acetaldehyde undergoes the aldol condensation with an alkaline catalyst. Mild hydrogenation to avoid dehydration leads to 1,3-butanediol. This is of historical

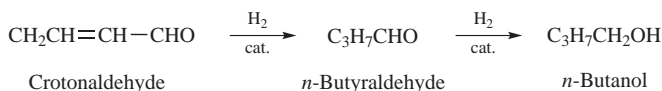
interest because on double dehydration it yields butadiene. This reaction was important during World War II when the monomer was needed with styrene for synthetic rubber.



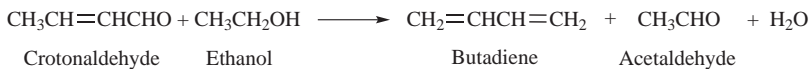
Dehydration of acetaldol in the presence of acetic acid gives crotonaldehyde, which can be oxidized to crotonic acid. The oxidation is a mild one, carried out at room temperature and slightly above atmospheric pressure. Crotonic acid is a specialty monomer for use in copolymers where pendant carboxyl groups are required.



Mild hydrogenation of crotonaldehyde yields *n*-butyraldehyde. More extensive hydrogenation attacks both the double bond and the aldehyde group to give *n*-butanol. Today, that route is obsolete and *n*-butanol comes from the hydroformylation of propylene (Section 6.9).

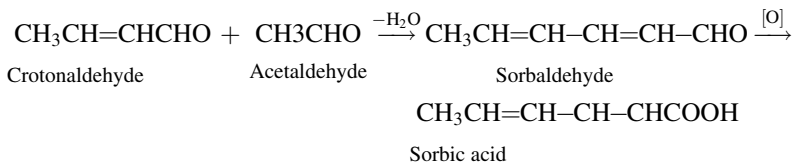


Crotonaldehyde, in a curious reaction with ethanol, gives butadiene and acetaldehyde.

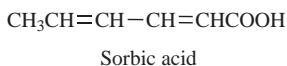
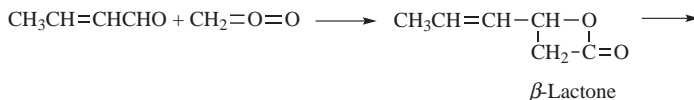


The latter can be recycled and converted to more crotonaldehyde. This synthesis of butadiene is still in use in India, Eastern Europe, and China, although it may well be phased out as petrochemical C₄ fractions become available.

Sorbic acid, 2,4-hexadienoic acid, in which both double bonds are *trans*, was originally made by two processes, one of which involves an aldol condensation between acetaldehyde and crotonaldehyde. The resulting sorbic aldehyde was then mildly oxidized to sorbic acid.



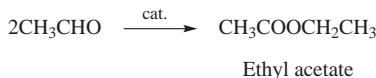
Selectivities are low since several aldol condensations can take place. In today's more sophisticated process, crotonaldehyde is reacted with ketene to give a β -lactone intermediate, which is hydrolyzed and dehydrated to sorbic acid.



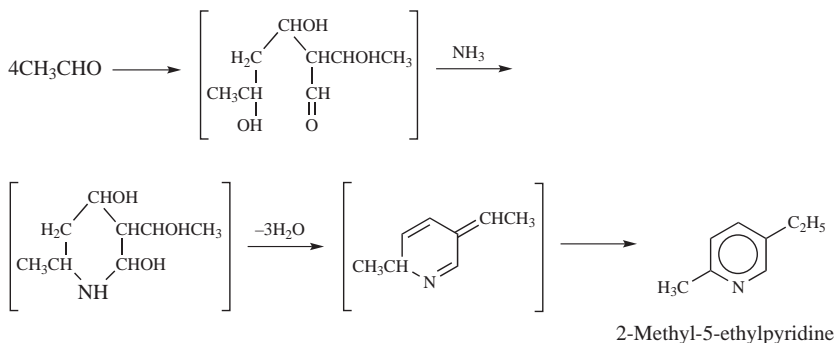
It is also possible to form an intermediate polyester by the self-polymerization of the lactone. It too will hydrolyze to sorbic acid. Ketene results from the pyrolysis of either acetone or acetic acid (Section 12.5.2.3).

Sorbic acid and its calcium and potassium salts (Section 5.11.1) are used like calcium propionate as preservatives for foods, especially baked goods.

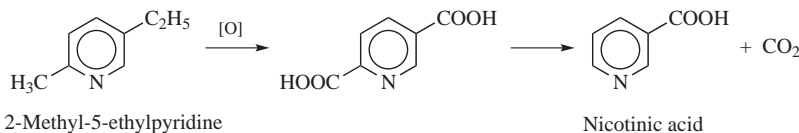
Acetaldehyde is a source of ethyl acetate by way of the Tishchenko reaction (Section 5.9). The catalyst is aluminum ethoxide.



Pyridine and some of its derivatives are still isolated from coal tar (Section 14.1). Synthetic pyridines from acetaldehyde have achieved importance. Ammonium acetate catalyzes the reaction of acetaldehyde and ammonia to 2-methyl-5-ethylpyridine by way of aldol condensations between four molecules of the aldehyde, followed by ring closure with ammonia. Triple dehydration brings about aromatization. The reaction takes place at high temperatures and pressures.

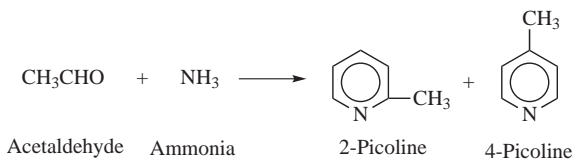


Oxidation of 2-methyl-5-ethylpyridine with nitric acid gives nicotinic acid by way of the decarboxylation of the intermediate dicarboxylic acid.

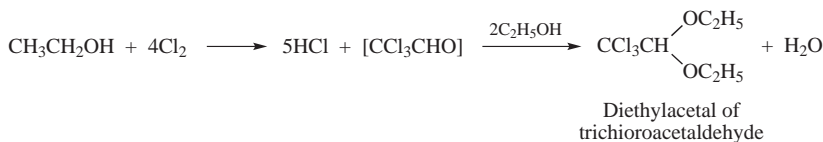


Nicotinic acid and its amide are both termed vitamin B₆. They lower lipid levels in the blood but their use is limited by side effects. They have a long established but more doubtful pharmaceutical use as peripheral vasodilators.

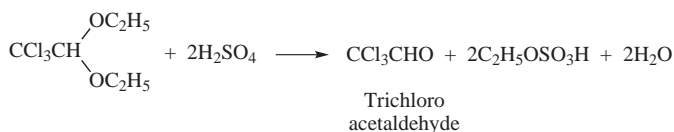
The reaction of acetaldehyde and formaldehyde in the presence of ammonia and a catalyst yields a mixture of pyridine and 3-picoline. Acetaldehyde and ammonia in a 3:1 ratio, when passed over various dehydration/dehydrogenation catalysts (e.g., PbO or CuO on alumina; ThO₂ on ZnO; or CdO on silica-alumina) give equimolar quantities of 2- and 4-picolines. 2-Picoline is a component of a coccidiostat; 4-picoline is a precursor of the antituberculosis drug isoniazid. Pyridines generally are of value as intermediates for herbicides, pesticides, and pharmaceuticals.



The chlorination of acetaldehyde yields trichloroacetaldehyde or chloral. In practice ethanol is chlorinated and is oxidized to the aldehyde in situ. In the presence of the HCl that forms, the trichloroacetaldehyde reacts with more ethanol to give the acetal.

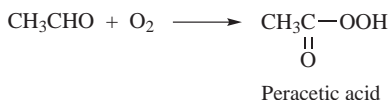


The reaction of the acetal with sulfuric acid provides the desired trichloroacetaldehyde and ethyl hydrogen sulfate.



The hydrate of chloral is stable and in the past has been useful as a soporific known in the vernacular as “knock-out” drops. The major use for trichloroacetaldehyde has been in DDT manufacture (Section 9.6).

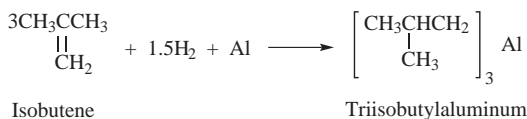
Peracetic acid (more appropriately peroxyacetic acid) is an intermediate in the oxidation of acetaldehyde to acetic acid (Section 5.5). If the oxidation is carried out at temperatures no higher than 40°C and at about 35 bar, it can be isolated.



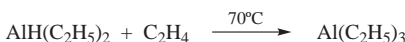
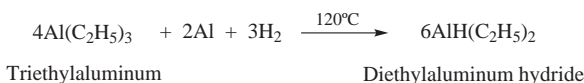
The alternative route to peracetic acid is the reaction of acetic acid with expensive hydrogen peroxide. Peracetic acid is used for several industrially important epoxidation reactions including the epoxidation of soybean oil (Section 15.9), α -olefins, and certain diunsaturates such as vinylcyclohexene (butadiene dimer, Section 7.1.6.1), which give reactive intermediates for the formation of materials resembling epoxy resins.

5.11.4 Metal Complexes

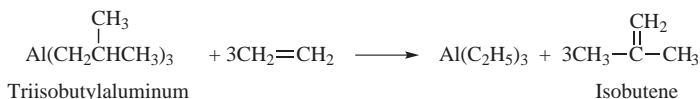
Triethylaluminum is important for the production of Ziegler alcohols and α -olefins (Section 3.3.2). Its combination with titanium salts provides the Ziegler–Natta catalyst (Sections 3.1 and 4.1). Triisobutylaluminum is an alternative. The process for preparing triethylaluminum is more complex than that for its higher analogs. Triisobutylaluminum results from the interaction of isobutane with hydrogen and aluminum at 150°C and 200 bar.



Triethylaluminum, on the other hand, cannot be made directly from ethylene, hydrogen, and aluminum because so high a temperature is required that the triethylaluminum formed reacts with more ethylene to give a mixture of higher alkyl aluminums. Thus it is necessary to react preformed triethylaluminum with aluminum powder and hydrogen to produce diethylaluminum hydride, which then reacts with more ethylene to yield more triethylaluminum than was used initially. Alternatively, both steps can be combined by simultaneous addition of hydrogen and ethylene to a mixture of triethylaluminum and aluminum powder.

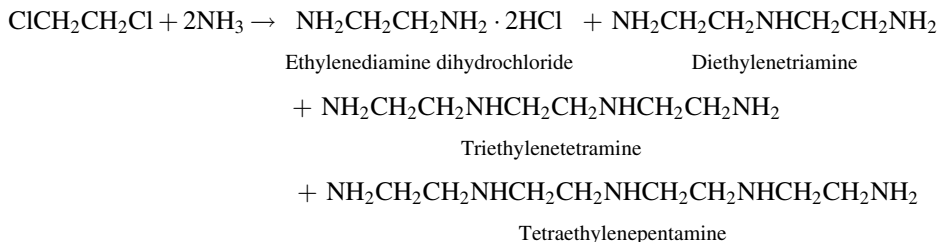


The exchange reaction between triisobutylaluminum and ethylene also gives triethylaluminum. Isobutene is recycled.

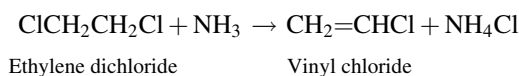


5.11.5 Ethylenediamine and Related Compounds

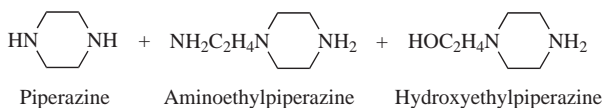
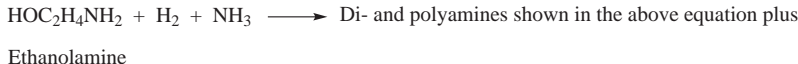
The reaction of ethylene dichloride (Section 5.4) with ammonia provides ethylenediamine and higher homologs including diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. The compounds form as hydrochlorides and are transformed to free bases with sodium hydroxide. The structures of the bases are shown in the equation. The reaction is carried out in the liquid phase with molar excesses of ammonia as great as 30:1 on a molar basis to minimize the formation of higher homologs. If the latter are required, less ammonia is used.



The above reaction gives vinyl chloride and organic-contaminated ammonium chloride as by-products, formed by the dehydrohalogenation of ethylene dichloride:

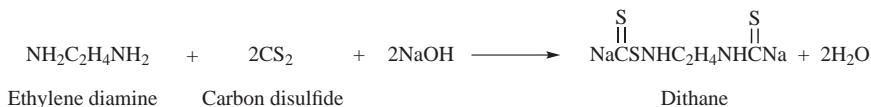


These present environmental problems. Accordingly, a process now more widely used has been devised for the production of ethyleneamines from ethanolamines (Section 5.11.6.4) and ammonia. Piperazine, aminoethylpiperazine, and hydroxyethylpiperazine are by-products.

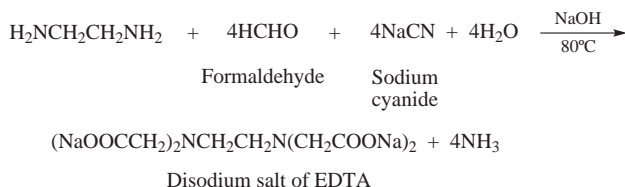


The reaction, a reductive amination, is carried out at high pressure in the vapor phase in the presence of hydrogen, with an amination catalyst such as nickel, cobalt, or copper. These polyamines are used as crosslinking agents for epoxy resins (Section 9.1.2.1) and for the preparation of low molecular weight fatty polyamide resins by reaction with so-called dimer acids (Section 15.5).

The reaction of ethylenediamine with carbon disulfide and sodium hydroxide gives the sodium salt of a bisdithiocarbonate, an important fungicide, Dithane.

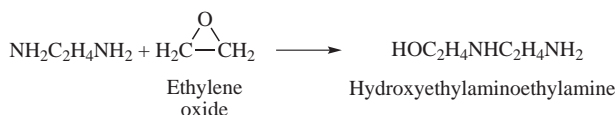


The reaction of ethylenediamine with formaldehyde and sodium cyanide in alcohol solution gives the sodium salt of ethylenediaminetetraacetic acid, an important chelating agent.

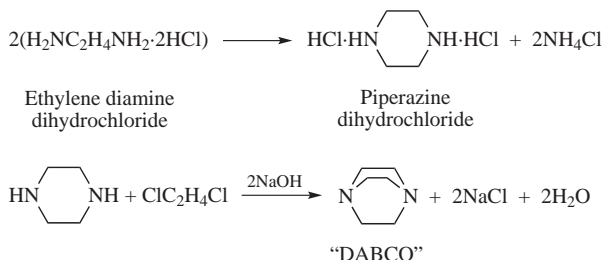


An alternative route involves the reaction of ethylenediamine with sodium chloroacetate. The product is a chelating agent both for alkaline earth and heavy metal ions.

Ethylenediamine reacts with ethylene oxide to provide hydroxyethylaminoethylamine, a textile finishing agent and an epoxy resin curing agent.



Piperazine dihydrochloride forms from the condensation of 2 moles of ethylenediamine dihydrochloride. Reaction of piperazine with ethylene dichloride yields triethylenediamine or DABCO, the acronym of its chemical name 1,4-diazabicyclo-(2,2,2)-octane. Triethylenediamine is an important catalyst for the interaction of isocyanates with polyols in urethane technology.²⁴



5.11.6 Ethylene Oxide and Ethylene Glycol Derivatives

5.11.6.1 Oligomers

Ethylene oxide oligomers – diethylene glycol and triethylene glycol – form during the hydrolysis of ethylene oxide to ethylene glycol (Section 5.7.1). If more of the oligomers is desired, less water is used for the hydrolysis, but normally more than enough by-product diethylene glycol is available. Additional triethylene glycol is produced by the reaction of ethylene oxide with ethylene glycol or diethylene glycol (Section 5.7.1).

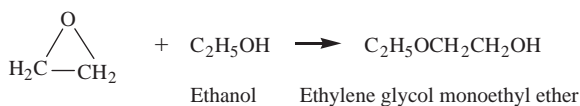
Di- and triethylene glycols are used in the manufacture of unsaturated polyesters (Section 11.1.3) to which they impart resilience and toughness. The ether linkages, however, increase water sensitivity. They are also used as solvents in polyurethane formulations and as the basis for textile chemicals, which serve as lubricants,

softeners, finishers, and dye assistants. They have been used for the extraction of aromatic hydrocarbons from aliphatic/aromatic mixtures such as catalytic reformat (Section 4.8) but sulfolane (Section 7.1.6.2) has largely replaced them. The glycols are useful for dehydration of natural gas, in the manufacture of plasticizers and surfactants, as tobacco humectants, and at a concentration no greater than 5% as antifreeze components. Triethylene glycol serves as a coalescing agent in water based paints to fuse solid particles of the vehicle into a film. The oligomeric polyethylene glycols are water soluble, waxy solids useful in cosmetic formulations and as ion coordination catalysts.

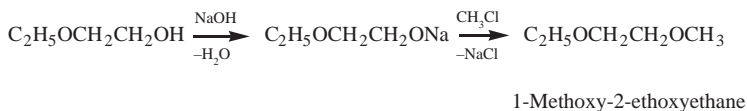
It is possible to obtain high molecular weight polyethylene glycols by the polymerization of ethylene oxide with an iron catalyst. These have not found extensive use. One of their interesting applications is to reduce the viscosity of water by decreasing its hydrogen bonding. Lower viscosity water enables easier flow through pipes particularly in fire fighting systems.

5.11.6.2 Glycol Ethers and Esters

Ethylene oxide reacts with alcohols to provide glycol ethers, the most important of which was ethylene glycol monoethyl ether (Cellosolve, Oxitol) the reaction product of ethanol and ethylene oxide. Oligomers, for the most part of little value, also form despite the use of large excesses of ethanol.



The glycol ethers may be esterified with acetic acid to give ethylene glycol ether acetates or further etherified by conversion of the hydroxyl to a sodium salt, which in turn will react with methyl chloride to give 1-methoxy-2-ethoxyethane.



Other commercial glycol ethers are based on methanol and butanols. The range is large; many of the commercially significant compounds are shown in Table 5.4, together with their chemical and trade names and structures. The consumer products in which they appear are also shown.

The ethylene glycol monomethyl and monoethyl ethers and their acetates, however, have been found to harm the reproductive and development process in mammals. Accordingly, very low emission levels in industry have been specified, and the compounds have not been used in consumer products for over 20 years. The question of their being banned generally has been debated for many years but as late as 2009 there had been no legislation. To some extent they are being replaced by related materials either with longer alkyl chains or based on propylene oxide (Section 6.8),

TABLE 5.4 Commercially Important Ethylene Glycol Ethers and Esters

Trivial Name	Chemical Name	Trade Names	Formula (R = -OCH ₂ CH ₂ -)	Direct Consumer End Uses
<i>Ethylene Glycol Ethers</i>				
Ethylene glycol monomethyl ether	2-Methoxyethanol	Methyl Cellosolve Glycol ether EM	HROCH ₃	None
Ethylene glycol monoethyl ether	2-Ethoxyethanol	Cellosolve Glycol ether EE	HR OC ₂ H ₅	None
Ethylene glycol monopropyl ether	2-Propoxyethanol		HR OC ₃ H ₇	Paints/coatings, cleaners, solvents
Ethylene glycol monobutyl ether	2- <i>n</i> -Butoxyethanol	Eastman EB Butyl Cellosolve Dowanol EB Butyl oxitol EB Hexyl Cellosolve	HR OC ₄ H ₉	Paints/coatings, cleaners, solvents, polishes
Ethylene glycol monohexyl ether	2-Hexoxyethanol		HR OC ₆ H ₁₃	Cleaners
Ethylene glycol monophenyl ether	2-Phenoxyethanol	Dowanol EPH	HR OC ₆ H ₅	Paints/coatings, cleaners, dyes
Diethylene glycol monomethyl ether	2-(2-Methoxyethoxy)ethanol	Eastman DM Methyl carbitol Dowanol DM Glycol ether DM	HRROCH ₃	Paints/coatings, solvents
Diethylene glycol monoethyl ether	2-(2-Ethoxyethoxy)ethanol	Eastman DE Carbitol low gravity Glycol ether DE	HRRO C ₂ H ₅	Hair colorant, floor polish, paints/coatings, cleaners, solvents
Diethylene glycol monopropyl ether	2-(2-Propoxyethoxy)ethanol	Eastman DP	HRRO C ₃ H ₇	Floor polish Brake fluids

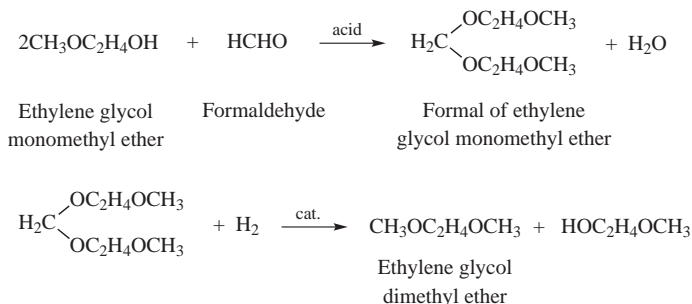
(continued)

TABLE 5.4 (Continued)

Trivial Name	Chemical Name	Trade Names	Formula (R = —OCH ₂ CH ₂ —)	Direct Consumer End Uses
Diethylene glycol monobutyl ether	2-(2-Butoxyethoxy)ethanol	Eastman DB Butyl Carbitol Dowanol DB	HRROC ₄ H ₉	Paints/coatings, cleaners, solvents, brake fluids
Diethylene glycol monohexyl ether	2-(2-Hexoxyethoxy)ethanol	n-Hexyl Carbitol	HRROC ₆ H ₁₃	Cleaners
Triethylene glycol monomethyl ether	2-[2-(2-Methoxyethoxy)ethoxy]ethanol	Methoxytriglycol Glycol ether TM	HRRROCH ₃	Brake fluids
Triethylene glycol monoethyl ether	2-[2-(2-Ethoxyethoxy)ethoxy]ethanol	Ethoxytriglycol Eastman DTE Glycol ether TE	HRRROC ₂ H ₅	Brake fluids
Triethylene glycol monopropyl ether	2-[2-(2-Propoxyethoxy)ethoxy]ethanol	Eastman DTP	HRRROC ₃ H ₇	Brake fluids
Triethylene glycol monobutyl ether	2-[2-(2- <i>n</i> -Butoxyethoxy)ethoxy]ethanol	Butoxytriglycol Eastman DTB Glycol ether DTP	HRRROC ₄ H ₉	Brake fluids
<i>Ethylene Glycol Ether Acetates</i>				
Ethylene glycol monoethyl ether acetate	2-Ethoxyethyl acetate	Glycol ether EE acetate	CH ₃ COROC ₂ H ₅	Solvents
Ethylene glycol monobutyl ether acetate	2- <i>n</i> -Butoxyethyl acetate	Eastman EB acetate Butyl Cellosolve acetate Glycol ether EB acetate	CH ₃ COROC ₄ H ₉	Paints/coatings solvents
Diethylene glycol monoethyl ether acetate	2-(2-Ethoxyethoxy)ethyl acetate	Eastman DE acetate	CH ₃ CORROC ₂ H ₅	Paints/coatings solvents
Diethylene glycol monobutyl ether acetate	2-(2- <i>n</i> -Butoxyethoxy)ethyl acetate	Eastman DB acetate Glycol ether DB acetate Butyl Carbitol acetate	CH ₃ CORROC ₄ H ₉	Paints/coatings solvents

which may not be quite as good solvents because of their branched structure. The reduction of sperm count by glycol ethers has recently been alleged and challenged.²⁵

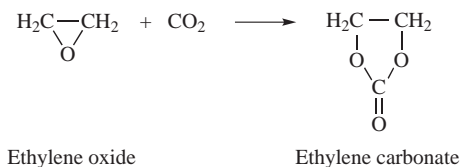
The glycol ethers and esters are water soluble. They are largely used as solvents for paints and coatings and as cleaning products, and in smaller volumes as solvents for printing inks, liquid cleaners, dyestuffs, and cosmetics. They are jet fuel deicing agents and brake fluids. Ethylene glycol monobutyl ether is particularly useful in water-borne coatings, which is the reason for its large production. Ethylene glycol dimethyl ether is used as an aprotic solvent (Section 5.11.6). A synthesis that decreases raw material costs by eliminating the need for sodium hydroxide and chlorine involves formation of the formal of the ether, which on hydrogenolysis yields 1 mole of the dimethyl ether and 1 mole of the starting material for recycle.



In 2006, the global market for glycol ethers (including propylene glycol-based ethers, the so-called P-series, Section 4.11) exceeded 13 million metric tons. The United States consumed about 30% of the ethylene glycol based materials (E-series), Western Europe 23%, and China 14%. Forty-six percent of the P-series ethers are consumed by Western Europe, followed by 25% in the United States and 10% in China.²⁶ A single compound – ethylene glycol monobutyl ether – accounts for about 60% of U.S. production, with diethylene glycol monobutyl ether and diethylene glycol monomethyl ether being the other major products.

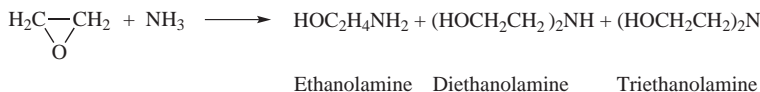
5.11.6.3 Ethylene Carbonate

Ethylene carbonate can be prepared by reaction of ethylene oxide and carbon dioxide with basic catalysts such as sodium hydroxide, and tertiary amines or quaternary ammonium compounds. The reaction is one of the few apart from the Kolbe synthesis, methanol formation (Section 12.5.2), and urea production (Section 12.5.1.3) in which carbon dioxide participates. The product is a high boiling, aprotic solvent useful in the synthesis of rubber chemicals and textile agents. Its use as an intermediate in ethylene glycol and dimethyl carbonate formation has been described (Section 5.7.1).



5.11.6.4 Aminoethyl Alcohols (Ethanolamines) and Derivatives

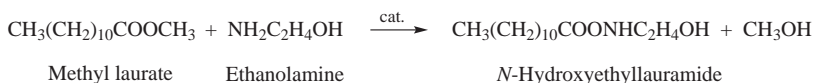
The interaction of ethylene oxide with ammonia provides ethanolamine, diethanolamine, and triethanolamine. The reaction is carried out with aqueous ammonia at about 100°C and 100 bar. If a high selectivity to ethanolamine is desired, excess ammonia is used. The formation of the di- and tri-products is favored because the rate of reaction of ammonia with ethanolamine is greater than with ethylene oxide.



A clever process has been devised by Nippon Shokuba I that uses a zeolite catalyst to enhance ethanolamine and diethanolamine yields, which are currently demanded by the market.²⁷ This is similar to toluene disproportionation, which provides a high yield of *p*-xylene (Section 10.1).

The end-use pattern of ethanolamines is shown in Figure 5.12. Global production is less than one million metric tons per year. Ethanolamines are used for the removal of acid gases from gaseous streams. Ethanolamine absorbs carbon dioxide and hydrogen sulfide but diethanolamine is required to absorb carbonyl sulfide. Being weakly basic, the ethanolamines form loose compounds with acid gases but these are decomposed by steam stripping and the ethanolamines are regenerated for recycle.

The reaction of fatty acid methyl esters such as methyl laurate with ethanolamine provides a fatty ethanolamide, widely used as a foam stabilizer in detergent formulations.



Diethanolamine (DEA) demand is rising. It is required for the synthesis of the herbicide, glyphosate, better known as Round-Up (Section 19.10) used as its isopropylamine salt. Treatment of DEA (**I**) with sodium hydroxide and copper gives

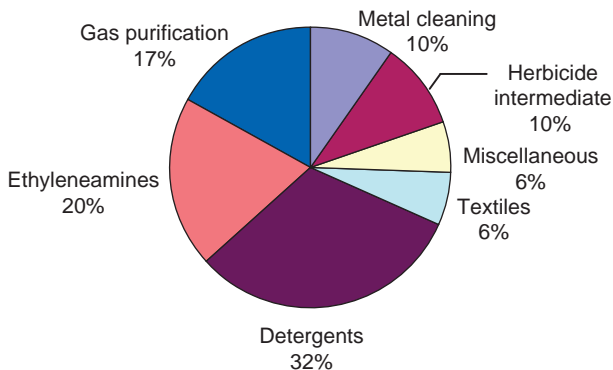
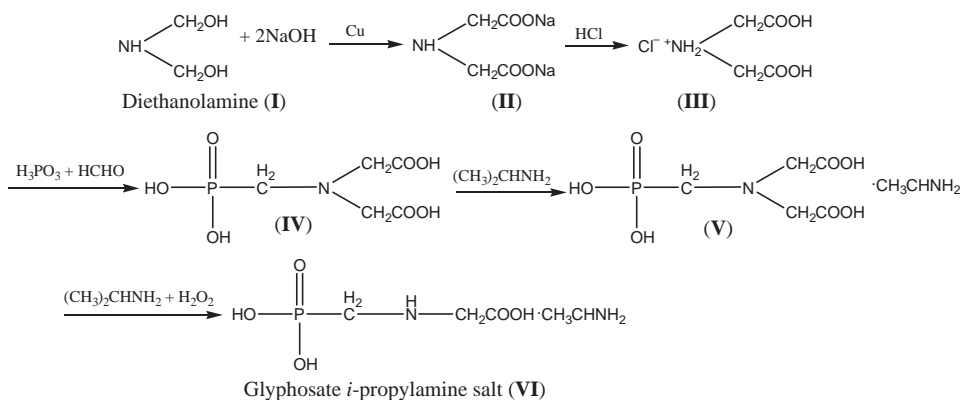


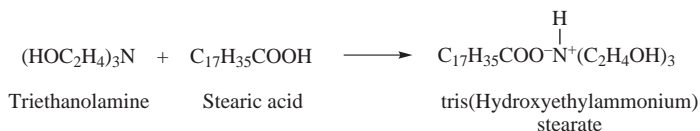
FIGURE 5.12 Ethanolamines end uses, 2008. (Source: Nexant Inc.)

the disodium iminodiacetate (**II**). Acidification gives the amine hydrochloride (**III**). Treatment with phosphonic acid and formaldehyde inserts the phosphonomethyl moiety to give (**IV**) and further treatment with isopropylamine and then isopropylamine and hydrogen peroxide or oxygen and a catalyst gives the isopropylamine salt of glyphosate.

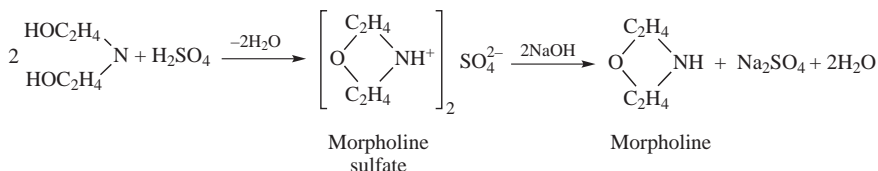


Monsanto has devised a “green” route to the iminodiacetate (**II**) described in Section 19.10.

Two other major herbicides 2,4-D(2,4-dichlorophenoxyacetic acid) and 2,4-DP(2,4-dichlorophenoxypropionic acid) are both marketed as diethanolamine salts. Triethanolamine’s major application is in the formation of a quaternary salt with fatty acids to provide a surfactant useful in dry cleaning and cosmetic formulations.

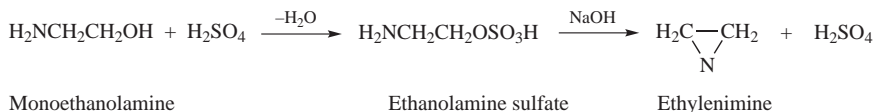


Morpholine results from the dehydration of diethanolamine with sulfuric acid, a sulfate forming, which on treatment with alkali provides the free base.

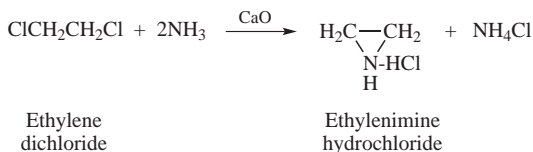


5.11.6.5 Ethyleneimine

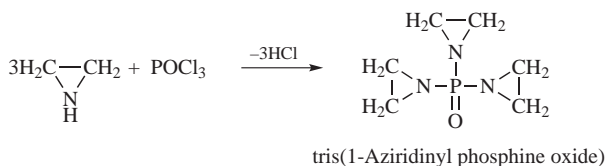
Ethyleneimine can be made from either ethanolamine or ethylene dichloride. The aminoalcohol is esterified with sulfuric acid and the resulting compound treated with a stoichiometric amount of sodium hydroxide to generate the imine.



Ethylene dichloride with ammonia in the presence of lime also yields ethylenimine.

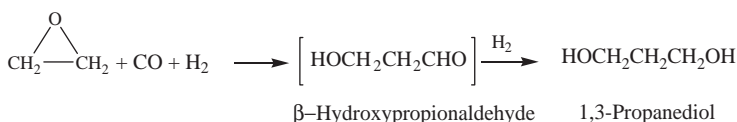


There is a large body of chemistry associated with ethylenimine most of which is beyond the scope of this volume. Most important is its polymerization to poly(ethylenimine), a cationic flocculent useful for the purification of waste waters, particularly water from paper manufacture. Reaction with phosphoryl trichloride, POCl_3 , provides tris(1-aziridinyl phosphine oxide), a reactive intermediate for use in imparting fire resistance and crease proofing to textiles. Ethylenimine and some of its derivatives are toxic and ecologically harmful.



5.11.6.6 1,3-Propanediol

It was known as early as the 1940s that polyester made from 1,3-propanediol and terephthalic acid or dimethyl terephthalate had unexpectedly good resilience and wear properties in comparison with its two and four carbon analogs, poly(ethylene terephthalate) and poly(butylene terephthalate). It had the potential to combine the stain resistance inherent in polyesters with the resilience and wear resistance of nylon. This phenomenon is sometimes termed the “odd carbon effect.” The unique blend of properties in poly(trimethylene terephthalate) should find application in fibers for carpets and apparel. This finding lay dormant for over 50 years as there was no low cost way to make 1,3-propanediol. In the mid-1990s, however, Shell developed catalysts that could combine syngas (mixtures of hydrogen and carbon monoxide) with ethylene oxide to give 1,3-propanediol in high yield. The chemistry goes through intermediate formation of β -hydroxypropionaldehyde. Shell has indicated they can carry out this reaction in one or two steps.

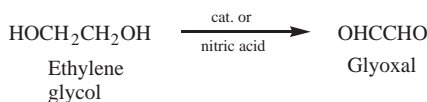


By analogy with ethylene and butylene, the polyester based on propanediol should be called poly(propylene terephthalate). The reason that Shell prefers poly(trimethylene terephthalate) is that polypropylene, in the carpet business, infers “cheap” and Shell did not want any confusion on this point so they came up with poly(trimethylene terephthalate).

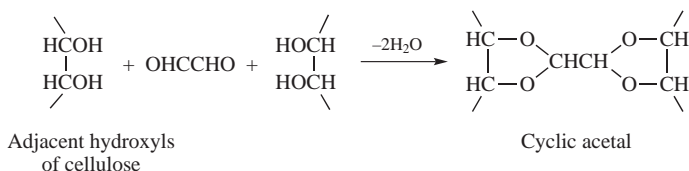
In 1999, Shell constructed a 73,000 metric tons per year 1,3-propanediol plant in Geismar, Louisiana. A 90,000 metric tons per year poly(trimethylene terephthalate) plant, built jointly by Shell and Soci  t   G  n  rale de Financement du Qu  bec (SGF), near Montreal, came on stream in 2004. DuPont did not abandon this market to Shell and purchased old acrolein-based technology from Degussa to supply developmental quantities of 1,3-propanediol (Section 6.11.4) Dupont’s real objective, however, was to develop a glucose-based biotech route to this monomer (Section 16.3). The product, which is corn-based, is called Sorona[®].

5.11.6.7 Ethylene Glycol Derivatives

The gas phase oxidation of ethylene glycol at 300  C yields glyoxal. Catalysts are silver or copper inhibited with halide additives to prevent total oxidation of the glycol. Alternatively, acetaldehyde can be oxidized with nitric acid less selectively to give glyoxal and a number of by-products including glyoxylic acid, OHCCOOH.



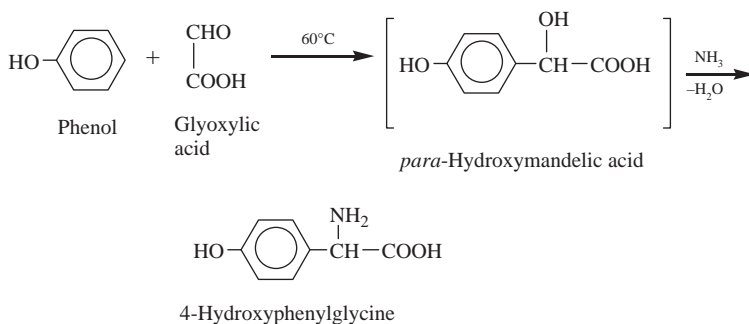
This is the major product when the oxidation is carried out at a higher temperature. It was at one time important in the synthesis of ethylene glycol (Section 5.7.1). Since anhydrous glyoxal polymerizes readily, it is sold as a hydrate. In textile finishing it functions as a shrinkproofing agent by crosslinking the cellulose chains of cotton through the formation of cyclic acetals with adjacent hydroxyl groups.



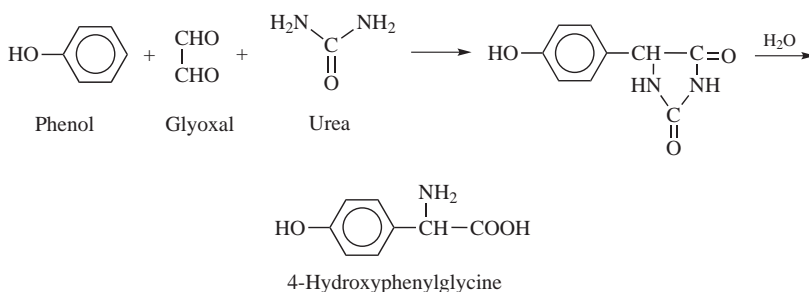
Its ability to react with cellulose also means that it lends wet strength to paper and increases its absorbency. It insolubilizes starch and protein and has been used as a reducing agent in the process of silvering mirrors. It reacts with amino groups and hence insolubilizes casein and animal glues. It is used to immobilize enzymes by bonding both to them and a substrate such as glass. Glyoxal mixed with formaldehyde is the basis for embalming fluid.

Glyoxal and glyoxylic acid are both used in the synthesis of 4-hydroxyphenyl-glycine, the side chain precursor in the manufacture of ampicillin. In one process – a modified Mannich reaction – phenol in aqueous ammonia reacts with glyoxylic acid

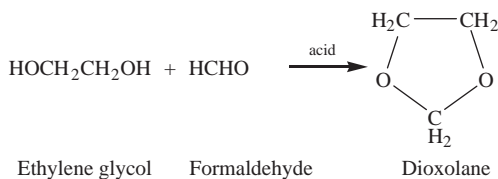
to give 4-hydroxyphenylglycine, presumably via the intermediate *p*-hydroxymandelic acid.



In the second method, phenol, glyoxal and urea react to give a hydroxyphenylhydantoin that is hydrolyzed by water to 4-hydroxyphenylglycine.

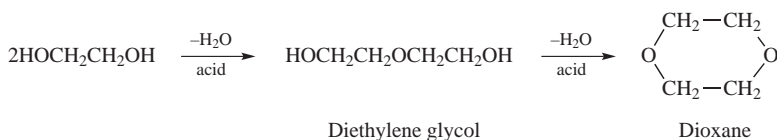


Dioxolane is related to ethylene carbonate (Section 5.11.6.3) and is the acetal from the acid-catalyzed reaction of ethylene glycol and formaldehyde.



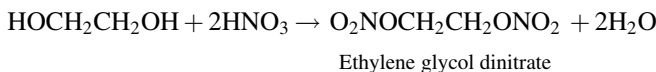
It is a comonomer in the formation of polyacetal polymers for which the major monomer is formaldehyde. It is also a strong aprotic solvent. Being an acetal, it is unstable in strong acid.

Another ethylene glycol derivative is 1,4-dioxane, which results from the dehydration of ethylene glycol with dilute sulfuric acid. Presumably, diethylene glycol forms as an intermediate and cyclizes to dioxane, since diethylene glycol may also be used as the starting material.



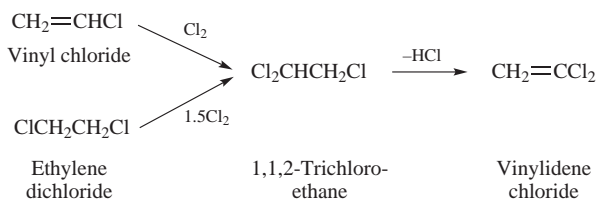
Ethylene oxide, ethylene chlorohydrin, or 2,2-dichlorodiethyl ether (prepared by treating ethylene chlorohydrin with sulfuric acid) all condense to form 1,4-dioxane. Dioxane's major use is as a solvent, but care must be exercised because it readily forms explosive peroxides.

Ethylene glycol can be nitrated to form ethylene glycol dinitrate, useful as a freeze inhibitor for explosives.



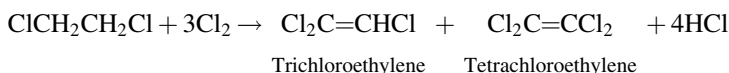
5.11.7 Vinyl Chloride and Ethylene Dichloride Derivatives

Vinyl chloride is the basis for other chlorinated compounds. Vinylidene chloride (1,1-dichloroethylene) results from the chlorination of vinyl chloride followed by dehydrohalogenation. The intermediate 1,1,2-trichloroethane can also be made by chlorinating ethylene dichloride:



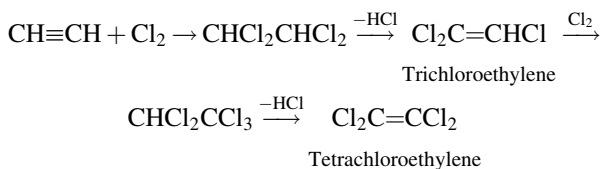
Vinylidene chloride is the basis for "Saran," which is a copolymer of 85% vinylidene chloride with 15% vinyl chloride. The polymer has high tensile strength, which makes possible the formation of thin films whose electrostatic properties cause it to cling and assume the shape of the products, primarily food, which it protects. Poly(vinylidene chloride) films are clear because they are biaxially oriented; that is, they are stretched in two directions simultaneously. The polymer is also used as a coating for nitrocellulose and polypropylene films to impart air and water impermeability.

The direct chlorination of ethylene dichloride gives a mixture of trichloroethylene and tetrachloroethylene in addition to 1,1,2-trichloroethane, mentioned above. The reaction is catalyzed by KCl/AlCl₃ or activated carbon:



To avoid waste of the quantities of hydrogen chloride by-product (the above equation is not balanced), oxychlorination can be used as it is in vinyl chloride manufacture (Section 5.4). The mechanism of the process, however, is somewhat different since it makes use of ethylene dichloride and chlorine in the presence of oxygen with a cupric chloride catalyst. In the vinyl chloride process, cupric chloride is used as a source of chlorine. In this process, chlorine, oxygen, and ethylene dichloride react to provide tri- and tetrachloroethylene and water. The hydrogen chloride which forms presumably oxidizes immediately to chlorine for further chlorination.

An obsolete synthesis of tri- and tetrachloroethylene started with acetylene (Section 12.3).

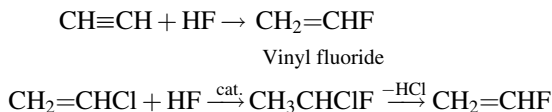


Trichloroethylene is used as a solvent and as a degreasing agent in metal working. In 2001, 235 million pounds (lb) were consumed. Tetrachloroethylene, also called perchloroethylene, is used to extract fats and oils and is the major solvent used in dry cleaning. Both solvents, however, are in jeopardy because of toxicity and ecological problems. Demand for tetrachloroethylene peaked in the 1980s and in Western Europe between 1996 and 2001. For example, demand for trichloroethylene dropped from 101,000 to 63,000 metric tons and for perchloroethylene from 85,000 to 67,000 metric tons.²⁸ The decline in demand can be attributed to use of tighter equipment and solvent recovery in the dry cleaning and metal cleaning industries and the phaseout of CFC 113 (trichlorotrifluoroethane) under the Montreal Protocol. A substitute for perchloroethylene in dry cleaning is liquid carbon dioxide. It is environmentally friendly, but only about 1% of the dry cleaners in the United States currently use it because the equipment is more expensive. In Europe, there are even fewer, but some exist.²⁹

Linde has been developing a proprietary carbon dioxide based solvent containing boosters – probably fluorine- or silicone-based surfactants.

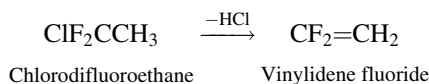
5.11.8 Vinyl Fluoride and Vinylidene Fluoride

Vinyl fluoride can be prepared either from acetylene (Section 12.3.2) or from vinyl chloride. In the latter process, vinyl chloride is treated with HF with a mercury salt or metallic fluoride catalyst to give an addition product, which on dehydrohalogenation yields vinyl fluoride.

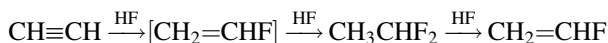


The noncatalyzed addition of HF to vinyl chloride proceeds at mild temperatures and pressures. Dehydrochlorination at 500–600°C with copper powder and Cu–Ni catalyst, or in special steel tubes, yields vinyl fluoride. A by-product, 1,1-difluoroethane, can be converted to additional vinyl fluoride by dehydrofluorination. Vinyl fluoride's major use is for free radical polymerization to poly(vinyl fluoride) with peroxide initiation. Films of this polymer have excellent resistance to weathering, ultraviolet light, chemicals, and solvents.

Vinylidene fluoride results from the dehydrochlorination of 1,1,1-chlorodifluoroethane.



Either alkali or heat is used. The precursor results from the addition of 2 moles of HF to acetylene followed by dehydrofluorination.

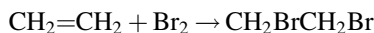


Vinylidene fluoride undergoes free radical polymerization to poly(vinylidene fluoride) which, unlike polytetrafluoroethylene (“Teflon”), may be molded by conventional techniques. It is useful for the preparation of high temperature wire insulation and heat-shrinkable tubing. As an emulsion it is used to coat metal for building panels.

Tetrafluoroethylene is not produced from ethylene but from methyl chloride and is described in Section 12.2.

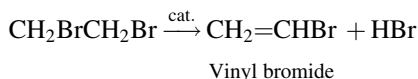
5.11.9 Ethylene Dibromide

Ethylene dibromide results from direct addition of bromine to ethylene.

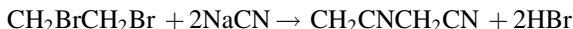


This reaction at one time provided the major outlet for bromine. Ethylene dibromide was used as a lead scavenger in leaded gasoline. The lead tetraethyl that served as an octane improver would otherwise have been oxidized to nonvolatile lead oxide, which would have accumulated in the engine. Addition of ethylene dibromide meant that lead bromide was formed, which was volatile enough to be swept out of the cylinders. This application became obsolete in the United States in the early 1990s. Ethylene dibromide is also a fumigant for soil and grain, but its use was prohibited in the United States in 1984 because of toxicity problems. Declining consumption has meant that a phase transfer catalytic route to ethylene dibromide was never commercialized³⁰ (Section 18.10).

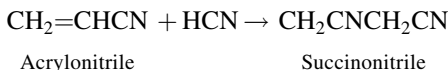
Dehydrobromination of ethylene dibromide yields vinyl bromide, used in small quantities in the formulation of fire retardants for carpet textiles.



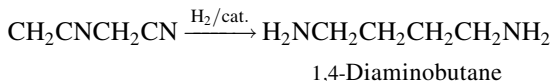
Reaction of ethylene dibromide with sodium cyanide gives succinonitrile, an aprotic solvent.



A better synthesis, if hydrogen cyanide is available, involves the addition of that compound to the active double bond in acrylonitrile. Triethylamine serves as catalyst.



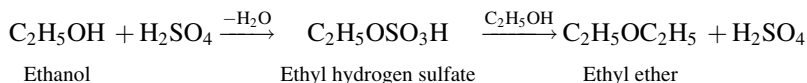
Hydrogenation of succinonitrile gives 1,4-diaminobutane:



1,4-Diaminobutane reacts with adipic acid to give nylon 46, a development product that came on the market in the mid-1980s. Nylon 46 has more amide groups than nylon 66 (Section 9.2.1.1) per equivalent of molecular weight. Accordingly, there is more opportunity for hydrogen bonding, which leads to greater tensile strength and higher melting point. On the other hand, the greater concentration of amide groups provides greater moisture sensitivity.

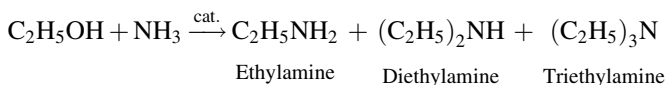
5.11.10 Ethanol Derivatives

Ethyl ether is prepared from ethanol by reaction with sulfuric acid (Section 5.8) to form ethyl hydrogen sulfate, which is transformed to diethyl ether by heating with more alcohol at 140–150°C, a temperature slightly below that at which it decomposes to ethylene. Ethyl ether is an important laboratory solvent and was at one time used as an anesthetic.

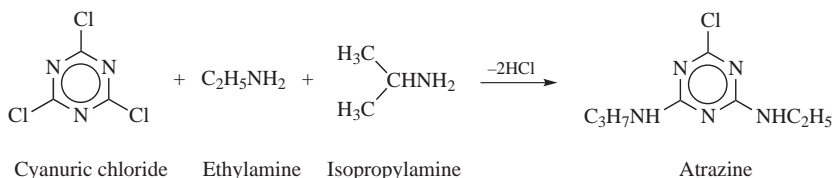


Ethylamines result when ethanol and ammonia are passed over a dehydration catalyst such as alumina or a mixture of silica and alumina. Amines and water are removed and

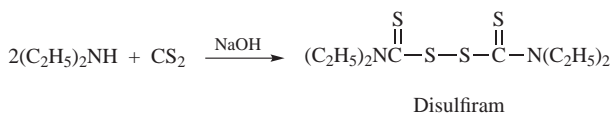
unreacted ammonia and ethanol recycled. The ratio of ammonia to alcohol is varied from 2:1 to 6:1 depending on the mix of amines required.



The ethylamines are used at a much lower level than the methylamines. Ethylamine finds its largest use in the preparation of herbicides by reaction with cyanuric chloride and isopropylamine. An ethylaminoisopropylamino-substituted chlorotriazine results, which is the herbicide atrazine.



Diethylamine with carbon disulfide and sodium hydroxide gives tetraethyl thiuram disulfide or disulfiram:



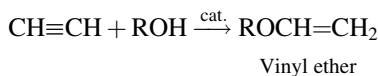
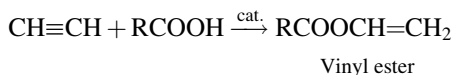
This compound is a rubber cure accelerator but is better known as “Antabuse,” a pharmaceutical used in the treatment of alcoholism.

5.11.11 Vinyl Esters and Ethers

One synthesis for ethyl acetate involves the direct addition of acetic acid to ethylene (Section 5.9):

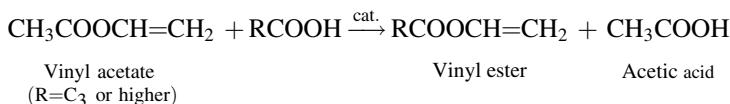


Analogously, vinyl esters of higher acids are prepared by their addition to acetylene. Vinyl ethers result from the interaction of alcohols and acetylene.



Vinyl esters may also be prepared by an exchange reaction in which an acid higher than acetic reacts with vinyl acetate in the presence of a catalyst. The vinyl acetate

process is a transesterification and is catalyzed by mercuric acetate with sulfuric acid, or by palladium chloride with lithium chloride.



Vinyl esters of fatty acids are used primarily as comonomers to impart flexibility to polymers based on vinyl chloride.

ENDNOTES

1. Nexant ChemSystems PERP report 08/09-1, *LDPE* (December, 2009).
2. See D. L. Lind and S. P. Saunders, *The Physics of Skiing*, American Institute of Physics, Woodbury, NY, 1997; and P. Walter, *Chem. Ind.* 26 July 2010. The K2 Skibook, *Some Information on the Technical Aspects of Skis*, K2 Corporation, Vashon, WA, is excellent but not generally available.
3. *Chemistry World*, 31 March 2008.
4. <http://en.wikipedia.org/wiki/Braskem>.
5. <http://www.biofuelstp.eu/butanol.html>.
6. Information on nylon–polyethylene mixtures made compatible by copolymers with polar and nonpolar functional groups is found in U.S. Patent 5,859,137 (12 January 1999) issued to DuPont. This patent describes the inclusion of unsaturated dibasic acids, primarily fumaric acid, with or without acrylic or methacrylic acid.
7. Phillips has issued many patents related to selective trimerization of ethylene to 1-hexene. Some of these are listed here: U.S. 5,523,507 (4 June 1996), U.S. 5,470,926 (28 November 1995), U.S. 5,451,645 (19 September 1995), U.S. 5,438,027 (1 August 1995) all assigned to Phillips. See also A. Brownstein, *ECN* 2–8 October 2000, pp. 29–30.
8. M. J. Overett et al., *J. Am. Chem. Soc.*, **127**, 10723, 2005.
9. *Chem. Eng. News*, 13 December 2010, p. 17.
10. The SHOP process has been described in detail by B. G. Reuben and H. A. Wittcoff, *J. Chem. Ed.*, **65**, 605, 1988.
11. Key patents covering EVC's ethane to VCM process are: WO 95/07249 (16 March 1995), WO 95/07250 (16 March 1995), WO 95/07251 (16 March 1995), and WO 95/07252 (16 March 1995) all to EVC Technology AG.
12. Parshall's statement about the Wacker reaction is to be found in his book *Homogeneous Catalysis*, Wiley, Hoboken, NJ, 1980, p. 102.
13. Showa Denko's process for the direct oxidation of ethylene to acetic acid is described in U.S. Patent 5,405,996 (11 April 1995) to Show Denko.
14. BP's fluidized bed reactor process for making vinyl acetate is described in U.S. Patent 6,180,821 (30 January 2001) and U.S. Patent 5,817,866 (6 October 1998) both to BP Chemicals Ltd.
15. U.S. Patent 6,448,432 to BP Chemicals, 10 September 2002.

16. <http://www.chemsystems.com/about/cs/news/items/Polyester%20Intermediates%20Market%20Dynamics.cfm>, <http://www.slideshare.net/josermbo/ssp>.
17. Union Carbide's process for converting ethylene oxide to ethylene glycol via the carbonate is described in five British patents: 2,011400; 2,011401; 2,011402; 2,010685, 2,010694.
18. The conversion with a vanadate or molybdate catalyst is described in International Patent Application WO85/04393 (10 October 1985) to Union Carbide.
19. <http://www.managers.org.cn/mag/doc/ucman201001/ucman20100104.pdf>, A. S. Abdul Rahim, M. A. Zariyawati, and H. O. Mohd Shahwahid, Short run and long run effects of the world crude oil prices on the Malaysian natural rubber and palm oil export prices, *Journal of US-China Public Administration*, **7**, 34–41, 2010.
20. The Dow approach for making styrene via butadiene cyclodimerization is described in U.S. Patent 5,276,257 (4 January 1994) to Dow Chemical.
21. <http://www.icis.com/Articles/2011/01/10/9424069/cl-based-advances-boost-feedstocks.html>.
22. The BP ethyl acetate process is described in *ECN*, 10–16 December 2001, p. 27.
23. <http://www.pjoes.com/pdf/17.5/727-731.pdf>.
24. <http://en.wikipedia.org/wiki/DABCO>.
25. N. Cherry, H. Moore, R. McNamee, A. Pacey, G. Burgess, J.-A. Clyma, M. Dipnall, H. Baillie, and A. Povey, Occupation and male infertility: glycol ethers and other exposures, *Occup. Environ. Med.*, **65** (10), 708, 2008. Their results are challenged in a letter to the same journal from P. J. Boogaard and G. M. H. Swaen, 11 July 2008.
26. <http://www.sriconsulting.com/CEH/Public/Reports/663.5000/>.
27. The Nippon Shokubai process is mentioned in *European Chemical News*, 9–15 April 2001, p. 43.
28. Chlorinated solvent sales data are taken from *Chem. Brit.* March 2003, p. 14. The ICI-Linde joint project is described in *Chem. Eng. News*, 2 September 2002, p. 12.
29. <http://www.washpoint.com/>.
30. B. G. Reuben, An industry under threat? *Chem. Ind.*, 547–552, 1999.

CHAPTER 6

Chemicals and Polymers from Propylene

After ethylene, the most important olefin is propylene. In 2009, the global demand for propylene for chemicals production was about 71 million metric tons. About 60% was produced as a coproduct of ethylene production in the steam cracking of gaseous feeds – ethane, propane, and butanes and liquid feeds, naphtha and gas oil (Section 4.5.1). About 33% was a by-product of catalytic cracking and about 7% came from new “on-purpose” propylene production technologies such as propane dehydrogenation (Section 6.1) and olefin metathesis (Section 6.1.1). This represents a shift from 2008 when the figures were 68% and 32%, with no on-purpose production. Future availability of propylene from catalytic cracking may be limited by slow growth in refineries and by a preference, especially in Asia, for hydrocrackers instead of fluidized bed catalytic crackers.

In addition to its role in the chemical industry, propylene has uses in a refinery. It can be reacted with isobutane to give alkylates for gasoline (Section 4.10) or, to a lesser extent, oligomerized to polygas (Section 4.9). In this respect propylene differs from ethylene, which has no nonchemical or fuel uses. Thus propylene has two major sources, that is, steam cracking and the refinery, and two basic sets of uses, in the refinery, for fuel and in the chemical industry.

Figure 6.1 shows the regional analysis of propylene capacity in 2009. Asia-Pacific had about as much propylene capacity as North America and Western Europe, put together. This is because Asia-Pacific producers use heavier feedstocks (naphtha and gas oil), compared with the lighter feedstock (natural gas liquids) used in the United States. Propylene demand is skyrocketing in Asia-Pacific, especially for polypropylene. This situation is changing rapidly with an extra 13–14 million metric tons/year of propylene capacity coming on stream in 2010 or shortly after. Similarly, Middle East propylene capacity is small compared with its ethylene capacity. This is because of the prevalence of ethane-based steam crackers in the Middle East, each affording little propylene. The Middle East’s capacity share will increase,

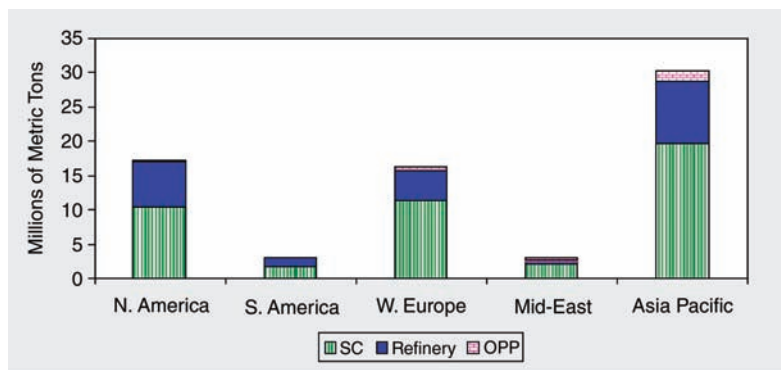


FIGURE 6.1 Propylene supplies by source and region (2009). (SC = steam cracking; OPP = on-purpose propylene.)

however, as there is a trend toward heavier feeds, increasing investment in fluidized catalytic cracking units and in propane dehydrogenation (Section 6.1).

Most natural gas contains about 2.5 times as much ethane as propane. On the other hand, catalytic cracking (Section 4.6) of higher petroleum fractions, which gives negligible amounts of ethylene, is a rich source of propylene although it is more dilute and thus more expensive to isolate than the propylene from steam cracking. The steam cracking of ethane, propane, butane, naphtha, or gas oil inevitably gives propylene as one of the coproducts, although the cracking of ethane gives so little it is often not isolated. The proportion of propylene depends on the feed (the higher the molecular weight the more is produced) and on severity of cracking. For naphtha and gas oil, it varies from 0.9 to 0.4 mol propylene per mol of ethylene as the cracking becomes more severe. A typical figure is about 0.5. This means that high severity (high temperature) cracking leads to a product rich in ethylene. Low severity cracking increases propylene content. Table 6.1 gives the yield of propylene and the propylene:ethylene ratio as a function of feedstock type and cracking severity.

For many years propylene was ethylene's ugly sister, a by-product that was used in the refinery, sold at a fraction above its fuel value or burned. Its availability coupled with its greater reactivity as compared to ethylene stimulated chemists' creativity, and many ingenious chemical reactions were developed including the ammoxidation route to acrylonitrile (Section 6.5) and the cumene-phenol process (Section 6.6). Historically, propylene's price was lower than that of ethylene, except under extraordinary circumstances. What changed everything was the discovery and continuing development of polypropylene. Figure 6.2 shows the demand pattern. Polypropylene has expanded from about one-sixth of the propylene market to only a little less than two-thirds.

Where was the propylene to come from? In 2008, in North America, which mainly cracks gaseous feedstocks, steam cracking provided only 10 million metric tons. Demand was for 16.2 million. The balance (32%) had to come from refineries. This was not met with enthusiasm. Refinery grade propylene is only about 70% pure (minimum level is 60%) and requires additional processing to reach chemical grade (93–94%) and polymer grade (>99.5%). Nevertheless, the industry coped.

TABLE 6.1 Overall Typical Propylene Yield from Representative Cracker Feedstocks

	Severity	Weight Percent of Feed	Propylene/Ethylene Weight Ratio
Ethane	High	1.5	0.019
Propane	High	13.7	0.304
<i>n</i> -Butane	High	15.9	0.376
Light naphtha	High	14.9	0.433
	Moderate	16.4	0.500
	Low	17.8	0.570
Full range naphtha	Moderate	15.7	0.512
Gas oil	Moderate	15.6	0.632

In Western Europe and Asia-Pacific, the main feedstock was naphtha, and there were few catalytic crackers. Thus steam crackers provided a greater yield of propylene but the refineries were of less help. In the Middle East, where mainly ethane is cracked, there is some on-purpose propylene capacity. The situation is summarized in Figure 6.1. The point is that supplies of propylene are constrained by the outputs of steam crackers (whose prime aim is to produce ethylene) and refineries (whose output is governed by gasoline demand).

Figure 6.3 shows the ratio of propylene to ethylene production in Western Europe and the United States, together with the ratio of West European contract prices. The production ratios drift only slowly upwards, reflecting the link between yields of the two materials. Between 1982 and 2002, the United States propylene/ethylene ratio remained between 50% and 60% but subsequently rose above the latter figure. The West European ratio was always higher because of heavier feedstocks, and rose

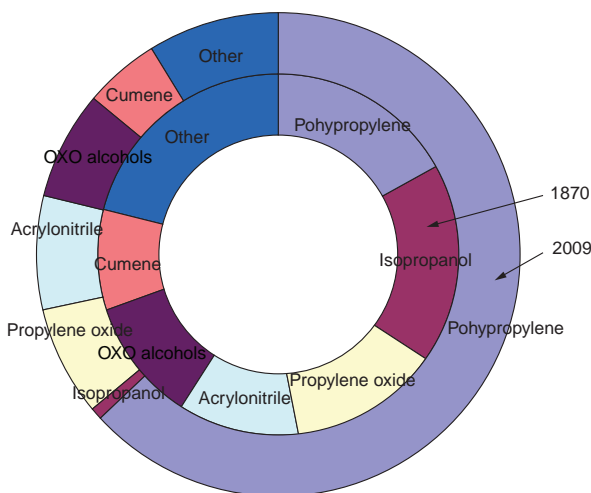


FIGURE 6.2 Global propylene demand pattern, 1970 and 2009; total 2009 production 71 million metric tons.

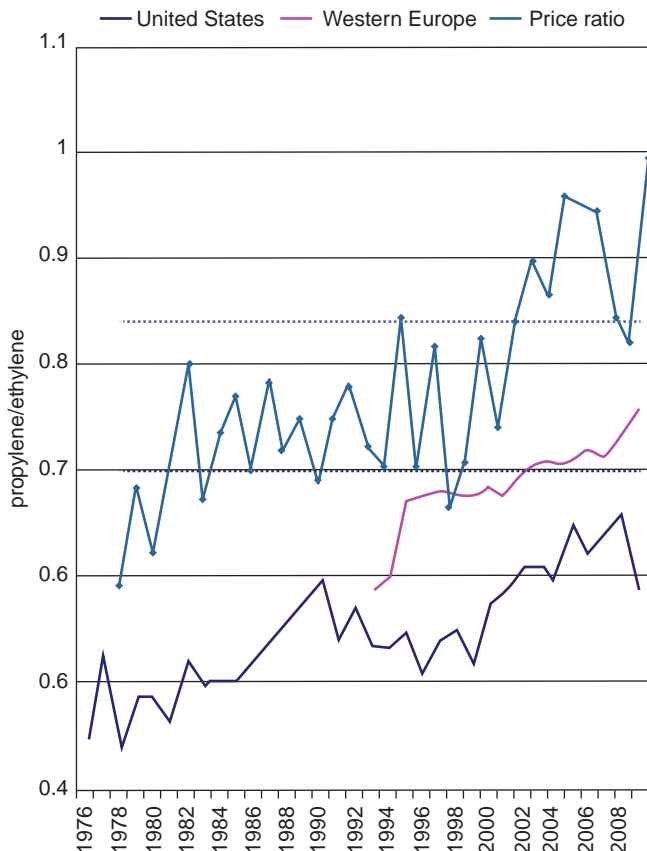


FIGURE 6.3 Propylene/ethylene production and price ratios. Between 1978 and 2008, the propylene/ethylene price ratio was normally between 0.7 and 0.85 and averaged 0.78.

significantly after 1994. Given the inelasticity of production, the ratio of the prices is more significant. It was below 0.7 before 1982 and the rise of polypropylene. In the 1980 and 1990s it varied between 0.7 and 0.85, and since 2002 has been above 0.85 and (the crack of gold for propylene producers) reached parity in 2010. This upward trend has led to efforts to improve propane dehydrogenation technology and to develop new so-called on-purpose routes to propylene. One of these, involving metathesis, was described in Section 4.14 and others are described below.

6.1 ON-PURPOSE PROPYLENE PRODUCTION TECHNOLOGIES AND PROPANE DEHYDROGENATION

Propane dehydrogenation process technology has been available for several decades but had never found much application because of unfavorable economics. As catalysts have improved, and the price of propylene has risen, it has found increased use.¹

The chemistry is simple on paper, involving catalytic abstraction of hydrogen from propane to give propylene. As is true of many endothermic reactions, however, the execution of it is more difficult. The major side reaction is cracking of propane to ethylene and methane, which, in turn, leads to hydrogenation of the ethylene to form ethane. Because the reaction is endothermic and accompanied by a positive entropy change, high temperatures favor greater conversions per pass but, above about 700°C, thermal pyrolysis becomes the dominant reaction. The optimum process conditions are determined by thermodynamic limitations, reaction kinetics, and economics of the conversion/selectivity relationship.

Propane dehydrogenation process technology is offered by several licensors including UOP, ABB Lummus, Linde/BASF, Snamprogetti/Yarsintez, and Krupp Uhde. The processes vary among the licensors in terms of reactor design, pressure, temperature, heating method, catalysts, and catalyst regeneration techniques. Table 6.2 shows all these parameters by licensor. The first propane dehydrogenation unit built was in Thailand in 1990 and a second in Northwest Europe in 1991. By 2010, 13 propane dehydrogenation plants were in operation making up about 3% of global propylene production. The size of the newest propane dehydrogenation units approaches 500,000 metric tons per year.

6.1.1 Propylene Via Enhanced Fluidized Catalytic Cracking

Propylene production from fluidized catalytic cracking (FCC) units can be increased by as much as 20–25% by changes in operating conditions and use of specially designed cracking catalysts. The increase in propylene is offset by decreased production of naphtha, which is usually the objective of FCC units. This approach is termed “Enhanced FCC,” although the earlier technologies were called Deep Catalytic Cracking (DCC).²

DCC was developed in China by the Research Institute of Petroleum Processing (RIPP) and Sinopec International. DCC utilizes fluid catalytic cracking principles and a proprietary catalyst to produce propylene and other light olefins from vacuum gas oil (VGO). RIPP has worked on the development of a zeolite catalyst for DCC for over 10 years. Several plants are operating in China currently, with more under construction. The first application outside China was a plant built by TPI in Rayong, Thailand in 1997.

Stone & Webster have the licensing rights to DCC outside China, but other companies have developed similar technologies. They include KBR, Petrobras, Lummus Technology/Indian Oil, Shell, ExxonMobil, UOP, Axens, KFUPM/Saudi Aramco/Nippon Oil, and Fortum Oy.

6.1.2 Propylene Via Selective C₄/C₅ Cracking

Selective C₄/C₅ cracking is similar to Phillip’s original olefin metathesis reaction, in that lower value olefins are upgraded to more valuable products. Unlike olefin metathesis, however, there is no need to use ethylene as one of the reactants. In fact small amounts of ethylene are produced. The chemistry is based on cracking C₄ and C₅ olefins over specially formulated shape-selective zeolite catalysts. The feed stream for

TABLE 6.2 Propane Dehydrogenation Process Characteristics

Licensors	UOP	Lummus	Linde-BASF	Snamprogetti-Yarsintez	Krupp Uhde
Process	Oleflex	Catofin	PDH	FBD	STAR
Catalyst	Platinum on alumina	Chromia-alumina	Chromia-alumina	Chromia-alumina with alkaline promoter	Platinum + tin on zinc aluminate
Pressure (bar)	1.38 at last reactor	0.13–0.68	1.4–2.1	1.2–1.5	2.1–4.2
Temperature (°C)	600–700	540–700	540	530–600	565–595
Partial pressure control	Hydrogen recycle	Vacuum	NA	NA	Steam
Heat method	Furnace reheat	Cyclic, coke burn-off	Fixed-bed multitube fixed heater	Coke burn-off in regenerator, supplemental fuel	Fixed-bed multitube fixed heater
Regeneration method	CCR	Cyclic	Cyclic in situ	Fluid bed	Cyclic in situ

NA = not available.

selective C_4/C_5 cracking can come from a steam cracker, raffinate-1 or raffinate-2, fluid catalytic cracking (FCC) C_4 streams or C_5 streams from steam cracker pyrolysis gasoline (Section 4.5.1). The only pretreatment needed is selective hydrogenation of all dienes. In addition to making relatively high amounts of propylene, selective C_4/C_5 cracking gives small amounts of light gases, some ethylene, and C_6 and heavier components suitable for gasoline. Kellogg Brown & Root are currently licensing their version of this technology, called Superflex, which was originally developed by ARCO Chemical. Sasol in South Africa has built the first Superflex unit and Jilin Chemical in China has licensed a second unit. ExxonMobil's version of this type of process is called Mobil Olefin Interconversion (MOI) process, while Lurgi's version is called Propylur. UOP and Total have jointly developed a process called Olefin Cracking Process (OCP).

Methanol to olefins (MTO) and more specifically methanol to propylene (MTP) is another on-purpose route to propylene. They are discussed in Sections 12.5.2.4 and 12.5.2.5.

6.2 MAIN POLYMERS AND CHEMICALS FROM PROPYLENE

The main polymers and chemicals made from propylene are shown in Figure 6.4. A breakdown of the various end uses for propylene is given in Figure 6.2. The largest end use by far is polypropylene followed by acrylonitrile, propylene oxide, and cumene.

The three types of reactions that ethylene undergoes – polymerization and oligomerization, oxidation, and “classical” reactions – apply here also. The unconventional chemistry in which one of ethylene's hydrogen atoms is replaced by chlorine, hydroxyl, and acetoxy to give vinyl chloride, acetaldehyde, and vinyl acetate is not repeated with propylene. Instead, propylene undergoes some unconventional chemistry of its own based on the stability of the vinyl moiety and the reactivity of the allylic hydrogen-containing methyl group. This active methyl can be oxidized directly to acrolein, allyl alcohol, acrylic acid, and, with ammonia, to acrylonitrile.

6.2.1 Propylene Polymers and Copolymers

Polypropylene is made with Ziegler–Natta catalysts (Section 5.1.1), typical of which is one developed by Himont and Mitsui Petrochemical, based on titanium tetrachloride with a Lewis base complex and a support of magnesium or manganese chloride. The Lewis base blocks nonstereospecific sites on the catalyst. A cocatalyst is used, which is a combination of an alkylaluminum such as triethyl aluminum with a Lewis base.

Polypropylene development provides a superb example of process improvement. As indicated in Section 17.3.10, polypropylene can exist in two crystalline forms, isotactic and syndiotactic, as well as in the amorphous or atactic form. Initially 1.2 kg of monomer was consumed per kg of isotactic polymer produced. Today only about 1.3% excess monomer is required. Modern catalysts will produce up to 70,000 kg of polymer per kg of catalyst, as compared to 1000–2000 pounds initially. This very high yield means that de-ashing or catalyst removal is not necessary. Similarly, an isotactic

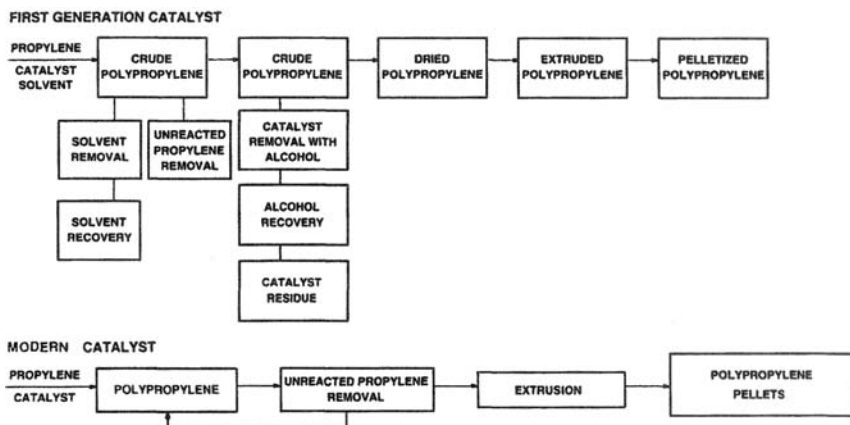


FIGURE 6.5 The modern catalyst simplifies the polypropylene plant.

polymer level of 97% is achieved, which makes unnecessary the removal of atactic material. The catalyst controls molecular weight distribution, important where a narrow weight distribution is required. The simplification of a polypropylene plant made possible by a modern catalyst as compared to the plant required by a first generation catalyst is shown in Figure 6.5. Significant engineering advancements have been made in polypropylene process technology in addition to catalyst advances. Single line process/extrusion capacity is now up to 550 metric tons per year.

With a Ziegler catalyst, polymerization takes place at 40–80°C. Polypropylene has been produced by slurry, solution, bulk, and vapor phase or fluid bed processes. In the slurry process, the catalyst is dispersed in an inert diluent such as hexane or heptane. The isotactic polymer that forms is insoluble in the hydrocarbon but the atactic material is soluble. Thus an in situ separation is effected.

In the solution process, the isotactic polymer is soluble in the solvent. This process has fallen into disuse because of the expense of solvent losses and the difficulty of removing all the solvent from the polymer. The bulk process makes use of pressures that maintain the propylene in liquid form. Atactic product is insoluble in liquid propylene, whereas the stereospecific polymer is soluble. The vapor phase or fluid bed process resembles one originally developed for polyethylene production (Section 5.1.3). This process became more popular in the 1990s. Bulk plants still comprise over half of all operating polypropylene plants, but vapor phase plants increased their share from about 15% in 1990 to almost 35% by 2009, and slurry plants account for about 6%.

There are fewer copolymers of propylene than there are of ethylene. Ethylene–propylene random copolymer elastomers have already been mentioned (Section 5.2.5). Also important is a block copolymer, comprising a polypropylene block and an ethylene–propylene copolymer block. This is made by first polymerizing propylene and then adding ethylene and more propylene, with the same catalyst as in the first step. The fresh material forms a random copolymer block that grafts onto the

original polypropylene block. The copolymer block plasticizes the polypropylene, improving its impact strength, which is poor at low temperatures. About 40% of polypropylene production is the copolymer. The homopolymer is used largely for fibers, although it may be molded if low temperature embrittlement is not a problem. Random copolymers of propylene with ethylene or 1-butene have poorer low temperature impact strengths because they are highly crystalline and therefore stiff. The block copolymer has lower crystallinity and greater flexibility, which gives it better low temperature properties.

Copolymers of propylene with olefins other than ethylene and with monomers such as vinyl chloride and styrene have been explored as possible replacements for expensive resins such as ABS (Section 7.1.4) and nylon.

The application of metallocene catalysts to polypropylene has lagged behind their application to polyethylene. Metallocene polypropylene has narrower molecular weight distribution, higher isotacticity, lower extractables, and slightly lower melt temperatures than conventional grades. It can be manufactured in conventional polypropylene plants, but the polymers are not a “drop-in” in end-use applications because the narrow molecular weight distribution leads to poorer processability. Second generation metallocene catalysts are expected to rectify this. Meanwhile metallocene polypropylene had 2–3% of the global polypropylene market in 2009, representing 1.4 million metric tons. The high cost of manufacture is also inhibiting market penetration.³

Metallocene catalysts also enable the production of syndiotactic polypropylene, which cannot be made with Ziegler–Natta catalysts. It has lower crystallinity and a lower melting point than conventional polypropylene but has high clarity and good impact strength. Atofina (Finaplas® 1571) and Mitsui operate small syndiotactic polypropylene plants. Market penetration has been low, indicating the difficulty of introducing a new product into a mature polymer market.

From 1995 to 2009 demand for polypropylene grew at a rate of 6.2% per year. Of all the polyolefins, only LLDPE has grown faster, notably 7.3% per year, over the same time period. Polypropylene’s major use is for injection molded products such as housings and parts for small and large domestic appliances, furniture, and office equipment. In automotive applications it is used for battery cases, interior trim, and air ducts. Injection molded packaging includes tubs for margarine, medicine bottles, and syringes. Reusable household food containers are made from copolymers. Polypropylene is used to make long-lived currency that resists counterfeiting. As of 2009, seven countries had at least one denomination of currency made from polypropylene. Polypropylene has a sufficiently high modulus (stiffness) and sufficiently low extensibility to be used for textile fibers and even for surgical sutures. It is found in clothing, particularly for sports, and as filament yarn in carpeting, upholstery, and automobile seats. An important application is in carpet backing. Polypropylene cloth can replace canvas in luggage and shoes. Thick polypropylene mats, either woven or nonwoven, are useful in stabilizing soil. They have found increasing use in road building to replace the rocks or aggregate normally combined with asphalt. Polypropylene film and sheet have greater strength and better high temperature properties than those from polyethylene, and oriented film can be used as a shrink wrap.

Polypropylene fiber is useful as an asbestos replacement when high temperature resistance is not required.

6.3 OLIGOMERIZATION

The oligomerization of propylene to highly branched olefin dimers, trimers, and tetramers (Fig. 6.4b), takes place in the presence of Friedel–Crafts catalysts such as sulfuric or phosphoric acids. A gasoline fraction (polygas) results (Section 4.9) from which the highly branched dimers, trimers, and tetramers can be isolated by fractional distillation, if desired. These oligomers were used for gasoline despite the double bonds that lead to tar formation in engines. The double bond, however, can be hydrogenated to give an aviation fuel, used in World War II notably for the British Spitfire. By the 1950s they had largely been replaced by alkylate (Section 4.10). Zeolites and pillared clays (Section 18.9) have been investigated as catalysts for oligomerization but have not found commercial application. The feed for oligomerization is usually catalytic cracker off-gases and includes not only propylene but the butenes, which are preferred because they form even more highly branched compounds with higher octane numbers. This technology practically fell into disuse with the development of alkylation. It has been revived to a small extent because the oligomers, especially the propylene/butene or butene-only based oligomers, are useful in unleaded gasoline. It was thought this approach could find increased importance if redundant MTBE plants started to convert their isobutene to branched octenes (Section 7.2.1), but gasoline consumption has dropped, discouraging this sort of activity.

A process, called “Dimersol,” developed by the Institut Français du Pétrole (now Axens) produces branched oligomers from propylene or propylene–ethylene blends using a nickel complex catalyst activated by an organometallic compound such as tri-*n*-propylaluminum. With *n*-butenes alone, or mixed with propylene, more nearly linear molecules result for petrochemical use such as conversion to oxo alcohols (Section 6.9) for plasticizers.

The important oligomers for chemical use are branched dodecene (propylene tetramer) and branched nonene (propylene trimer), octene (butenes dimer), heptene (dimer of propylene and butenes), diisobutene (dimer of isobutene), and hexene (propylene dimer). Propylene tetramer formerly was used for the alkylation of benzene to make a branched chain dodecylbenzene that was subsequently sulfonated to provide a nonbiodegradable surfactant. This application is now insignificant in the United States as more biodegradable detergents such as linear alkylbenzene sulfonates and alcohol ethoxylates (Section 9.4) have replaced them. Phenol may be alkylated with propylene trimer or tetramer to give nonylphenol and dodecylphenol, respectively. Both are used in lubricating oil additives. They react with ethylene oxide to give nonionic detergents.

Propylene trimer and tetramer and butenes dimer undergo the oxo reaction (Section 6.9) and the aldehydes can be hydrogenated to isodecanol, tridecanol, and nonanol, respectively. Their major use is as their phthalates, which are PVC plasticizers. The phthalates have been under attack since the 1960s for environmental reasons.

2-Methyl-1-pentene is a dimer of propylene produced with the aid of a tri-*n*-propylaluminum catalyst. It is the basis for an isoprene synthesis that was never commercialized (Section 8.2). Another dimer, 4-methyl-1-pentene, was developed by ICI as a monomer for a specialty polymer which, despite its crystallinity, is transparent, because the refractive indices of the crystalline and noncrystalline portions are the same. Therefore light is not reflected at crystal boundaries. The catalyst for the dimerization is a combination of sodium and potassium carbonate. The process was sold to Mitsui, which had manufactured the polymer. The monomer is finding some small use as a comonomer in LLDPE (Section 5.1.4).

6.4 ACRYLIC ACID

At the beginning of this chapter, we mentioned that propylene underwent some unconventional chemistry based on the stability of its vinyl moiety and the reactivity of its methyl group. This methyl group may be oxidized to a carboxyl group just as the methyl group of toluene may be oxidized to give benzoic acid. Similarly, the methyl groups of both toluene and propylene can be chlorinated and subjected to ammoxidation. The mechanisms that cause these reactions to take place with the two molecules are different and perhaps this is the reason why the similarity was not recognized earlier. The chlorination and conversion to an alcohol are discussed in Section 6.11.1, and the ammoxidation reaction is described in Section 6.5. The oxidation to an aldehyde and an acid is described here.

The oxidation of propylene gives acrolein first and then acrylic acid. There are several other routes to acrylic acid and its esters, all but one of which has, at one time or another, been commercial. They are shown in Figure 6.6.

Acrylonitrile hydrolysis (Fig. 6.6e) is an obvious route. It is economic if small amounts of acrylic acid are required and is still used by some acrylonitrile producers to make acrylic acid for captive use. Another route involves the reaction of hydrogen cyanide with ethylene oxide to give ethylene cyanohydrin, which may be simultaneously dehydrated and hydrolyzed with sulfuric acid [Fig. 6.6d(1)]. This process was last used in 1971. A third method involves the treatment of acetaldehyde with hydrocyanic acid to give a different cyanohydrin, which may be similarly dehydrated and hydrolyzed [Fig. 6.6d(2)]. This process too is obsolete.

Reaction 6.6e starts with ketene from the pyrolysis of acetic acid (Section 12.5.2.3). It reacts with formaldehyde to give β -propiolactone, which, on reaction with an alcohol, gives an acrylate ester directly. The high toxicity and the carcinogenicity of the lactone made this route unattractive.

Reaction 6.6b is a relic of the great days of acetylene chemistry. Acetylene is reacted with an alcohol and carbon monoxide in the presence of a nickel carbonyl catalyst to give an alkyl acrylate directly. The process, now obsolete, accounted for almost half of the total acrylic acid and ester production in the United States in 1976. It was still used in the United States in the early 1980s and was one of the last acetylene-based reactions to give way to modern chemistry.

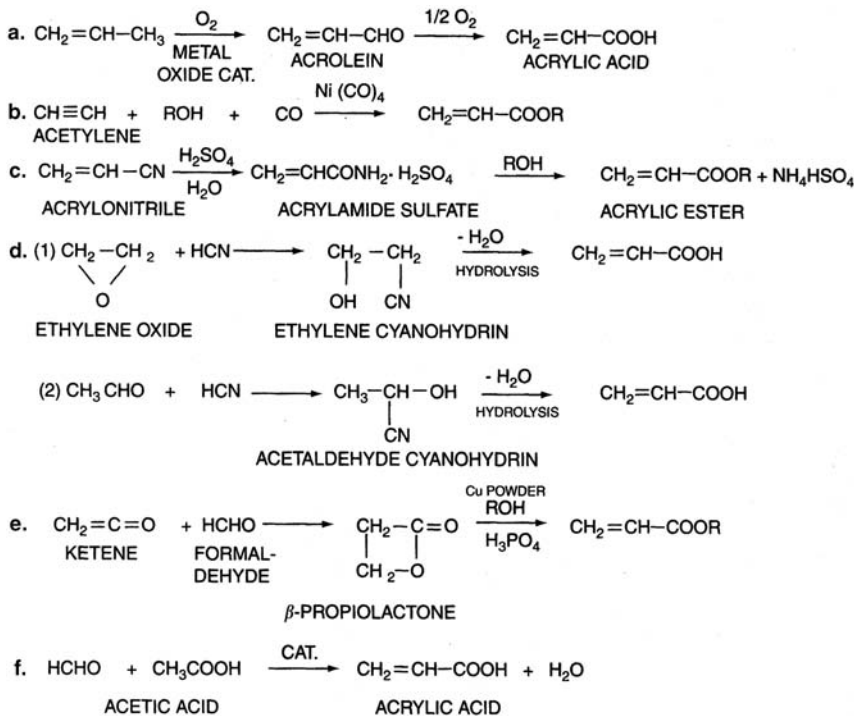


FIGURE 6.6 Acrylic acid: possible production methods.

Figure 6.6f shows a proposed process in which formaldehyde reacts with acetic acid to give acrylic acid, presumably by way of a hydroxymethyl intermediate. The process, although not commercialized, is of interest because it provides a route to acrylic acid from synthesis gas (Section 12.4) since acetic acid is made from carbon monoxide and methanol, which in turn is made from synthesis gas. Similarly, formaldehyde is made by the oxidation of methanol. The vapor phase reaction is carried out with a vanadium orthophosphate catalyst. Conversion is as high as 100% at approximately 60% selectivity. Formaldehyde is used in a similar way in a relatively new process for methyl methacrylate (Section 6.7.1).⁴

Propylene oxidation (Fig. 6.6a) is currently the preferred route. The two-step process yields acrolein as an intermediate that can be isolated if desired (Section 6.11.4). Optimum catalyst and temperatures are different for each of the two steps, the first step requiring a much higher temperature than the second. Molybdenum-based catalysts predominate and a typical catalyst for the first stage of the two-step conversion is $\text{Fe}_4\text{BiW}_2\text{Mo}_{10}\text{Si}_{1.35}\text{K}_{0.6}$. With this catalyst at 320°C, propylene conversion is 98% and acrolein (with some acrylic acid) selectivity is 96%. These results are typical of what can be achieved with modern sophisticated catalysts. In the second stage, a catalyst may be used comprising $\text{Mo}_{12}\text{V}_{4.6}\text{Cu}_{2.2}\text{Cr}_6\text{W}_{2.4}$. The catalyst is supported on alumina and at 220°C a 98% molar yield of acrylic acid is obtained.

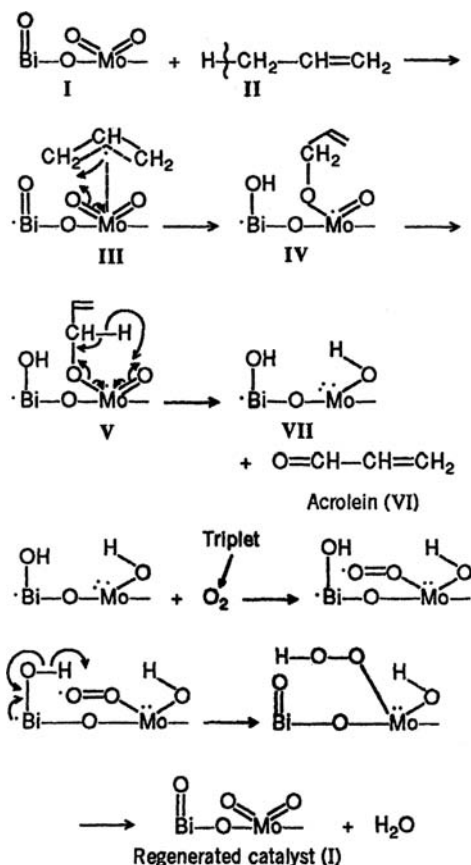


FIGURE 6.7 Mechanism of acrolein formation.

Figure 6.7 shows a proposed mechanism for the conversion of propylene to acrolein. The catalyst (I), a bismuth molybdate, abstracts a hydrogen from propylene (II) and pi-bonds the resulting radical (III). The formation of a carbon-oxygen bond (IV) and a hydride shift (V) leads to the formation of acrolein (VI) and a reduced form of the catalyst (VII). The catalyst is regenerated by reaction with oxygen as shown at the bottom of the figure.

The two major developers and licensors of the modern two-stage acrylic acid process are Japanese companies, Nippon Shokubai and Mitsubishi Chemical. Some licensees have further refined the catalyst systems, notably BASF, in order to improve operating characteristics. These improvements are proprietary and acrylic acid catalyst know-how is closely held, but all major producers are thought to obtain similar yields. The first stage oxidation reactor is a fixed bed tubular reactor with tubes that are about 5 meters long and 2–3 centimeters in diameter. The catalyst is packed into the tubes in three zones. The catalyst concentration increases as the reactants pass down the tube creating a uniform reaction rate throughout the reactor. The reactors are

cooled with molten salt that is circulated around the tubes. The second stage reactor is similar but with a different catalyst. The crude acrylic acid is quenched by absorption in water and isolated by solvent extraction. “Semipurified” acrylic acid is obtained in an initial distillation and this is suitable for making acrylic esters. Glacial acrylic acid is obtained by a second distillation. Acrylic acid is corrosive and corrosion-resistant materials are required in the distillation tower and all downstream handling equipment. Probably stainless steel is used for the piping and titanium-clad mild steel for the columns. Purification by crystallization is believed to be used by a few producers.

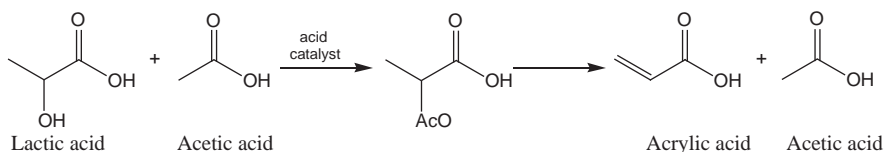
Several other routes to acrylic acid are under development. Direct propane oxidation to acrylic acid is one possibility. Companies that have worked in this area include Mitsubishi Rayon, Sumitomo Chemical, Sunoco, and Toagosei with patents having been issued to Arkema and BASF.⁵

Novomer, a start-up company, is developing a route to acrylic acid that involves the addition of carbon monoxide to ethylene oxide to give propiolactone. Propiolactone can be converted to acrylic acid by known technology (Fig. 6.6e).

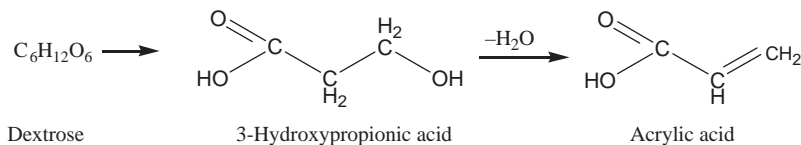
6.4.1 Biorenewable Processes to Acrylic Acid

There are several biotechnological processes in use or under development.⁶ A patent by Genomatica⁷ combines biosynthesis and chemical steps. Acrylic acid is produced by the cross-metathesis of fumaric acid (produced by the fermentation of a carbohydrate substrate such as glucose or sucrose) with ethylene in the presence of a Grubbs ruthenium catalyst.⁸

Another biotechnology route is based on lactic acid. Lactic acid (Section 16.6) reacts with acetic acid and/or acetic anhydride to give 2-acetoxypropionic acid, which is then deacetoxylyated to yield both acetic acid and acrylic acid.

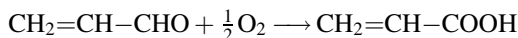
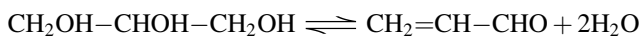


Cargill and Codexis spent five years devising a microbial conversion of dextrose and other carbohydrates to 3-hydroxypropionic acid. This is seen as a potential feedstock for a range of organic chemicals (Section 16.4.1). In this case, distillation in the presence of an undisclosed catalyst gives acrylic acid. Cargill and Novozymes were said to be building a plant.⁹



Arkema’s biotransformation route also involves either a single-step or two-step reaction. In the single-step process, glycerol is oxydehydrated in the presence of

molecular oxygen to give acrylic acid via an acrolein intermediate. The catalyst needs both to dehydrate and oxidize the glycerol.¹⁰



In the two-step process, glycerol is dehydrated to acrolein, which is then oxidized to acrylic acid.

Lactic acid (2-hydroxypropionic acid) can be made by fermentation and can be similarly dehydrated to acrylic acid.

6.4.2 Acrylic Acid Markets

The world production of acrylic acid in 2009 was about 3.9 million metric tons, with BASF (16%), Dow (now combined with Rohm & Haas) (13%), and Arkema (13%) the major producers. The U.S. consumption is currently about 27% of world production with Western Europe consuming 21% and Asia-Pacific 46%. Glacial acrylic acid is needed for making superabsorbent polymers (see below). This is a growth area and, in 2009, enjoyed 30% of the acrylics market. Fifty-five percent was converted to an important range of esters – methyl, ethyl, butyl acrylates – used largely in latices, and 2-ethylhexyl acrylate used as a homo- and copolymer. The remainder was used for detergent, flocculants, and other small end uses.¹¹

Acrylate esters are polymerized usually with comonomers, including methyl methacrylate and/or vinyl acetate. The butyl and 2-ethylhexyl/vinyl acetate copolymers, in the form of emulsions, are used in water-based paints, sometimes with other copolymers. This market accounts for about 30% of the use of all acrylates. They are also used in solvent-based coatings and, as copolymers with methacrylates, for product finishes such as thermosetting automotive topcoats. For this application, the acrylates are combined with melamine (Section 12.5.1.3). Acrylic coatings are prized for their decorative quality and their film durability, particularly out of doors, where their resistance to ultraviolet light is of benefit. Acrylic emulsions are also found in textile chemicals and adhesives, which are the second and third largest uses, as well as in paper coatings, binders for nonwoven fabrics, polishes, and leather coatings. Ethyl acrylate is important in leather treatment and methyl acrylate has found application as a comonomer in acrylic fiber production (Section 6.4.2) Thermoplastic acrylate coatings have been prized for automobile topcoats because they contribute the indefinable “depth” of the topcoat. They contain much more solvent than the thermosets, however, and have been phased out because of the contribution of the solvents to air pollution.

A two-package coating based on hydroxyl-containing acrylic copolymers (made with hydroxyethyl acrylate as one of the monomers) may be crosslinked with diisocyanates to give a hard thermoset polymer that cures at room or slightly elevated temperatures. It is the preferred vehicle for coatings for automobile refinishing.

A growing application for acrylic monomers is in ultraviolet-cured coatings and printing inks. Pentaerythritol (Section 5.11.3) tetraacrylate and oligomers of it are typical. They are applied to a substrate such as plywood for subsequent polymerization into a film by UV light. The films must be clear, since pigments absorb UV rays, and can be applied only to a horizontal surface. Printing inks based on acrylic monomer and oligomers can be cured by UV light because their low volume pigmentation does not seriously interfere with curing. Heavily pigmented coatings can be cured by electron beams, but the equipment is expensive and the process requires safety precautions.

Two applications for acrylic acid were developed in the mid-1980s that motivated expansion of acrylic acid production. One is the use of polyacrylic acid (prepared by the peroxide-induced free radical polymerization of acrylic acid) or an acrylic acid/maleic anhydride copolymer as a builder in detergents to replace phosphates for chelating of calcium and magnesium ions. Polyacrylates also serve as dispersing aids and inhibit soil redeposition.

The second use is as water-absorbing agents for disposable diapers and personal care products. The polymers are termed superabsorbent polymers (SAPs) because they can absorb over a thousand times their weight of water. A typical formulation comprises a copolymer of acrylic acid, sodium acrylate, and a small quantity of a crosslinking agent such as trimethylolpropane (Section 17.4.2) triacrylate. Crosslinking is necessary in order to impart salt stability to the gels. The global market for SAPs in 2009 was estimated at 1.2 million metric tons. End-use profile is dominated by baby diapers with almost 80% of the market. Other uses include adult incontinence pads and feminine hygiene products. Emerging applications are in agriculture, where SAPs are used for hydrogels for water retention in arid planting areas, medical wound dressings, cable wrap for underground telecommunication cables, fire protection, meat and fish wrap pads, and artificial snow. The major suppliers of SAPs are BASF, Dow, Nippon Shokubai, Stockhausen, and Sanyo.

Another type of water absorber, irreverently termed “superslurper,” is made from a starch graft polymer in which acrylonitrile is grafted onto starch to give long chains. Thereafter the nitrile groups are partially hydrolyzed to amide and carboxyl groups. Here too a small amount of a crosslinking agent – a polyfunctional acrylate or methacrylate – must be used to achieve stability of the gel in the presence of salts. Starch graft polymers may also be prepared with acrylamide and acrylic acid rather than acrylonitrile.

6.5 ACRYLONITRILE

Closely related to the direct oxidation of propylene to acrolein and acrylic acid is its oxidation in the presence of ammonia to give acrylonitrile (Fig. 6.4d). It is the second largest volume derivative of propylene. The process, developed by SOHIO in the United States and by Distillers Company in Great Britain, is known as ammoxidation. It excited much attention when discovered in the late 1950s, for there was no previous example of the formation of a C–N bond in this way. SOHIO and Distillers were

involved in a bitter patent battle in the 1960s until BP Chemicals acquired both companies. BP was the leading producer of acrylonitrile until 2006 when the business was sold to INEOS. Over 95% of all acrylonitrile is produced by the SOHIO process.

In the early 1960s ammoxidation displaced various processes for acrylonitrile production such as the addition of hydrogen cyanide to acetylene, the interaction of ethylene oxide with hydrogen cyanide followed by dehydration, and the reaction of propylene with nitric oxide. A bismuth phosphomolybdate catalyst was initially used in the United States. This was replaced by uranium bismuthate, which contained depleted uranium. This in turn has been superseded by proprietary catalysts used in the vapor phase that have increased the yield of acrylonitrile and boosted reactor throughput.

The catalysts are described in an extensive patent literature. Most of them reduce by-product acetonitrile production almost to zero, but by-product hydrogen cyanide is still produced. A typical catalyst contains silica-supported oxides of selenium, iron, and tellurium in ratios corresponding to $\text{OSe}_{1.0}\text{Fe}_{0.83}\text{TeO}_{0.68}\text{O}_x$. This catalyst gives 100% conversion of propylene with 86.9% selectivity to acrylonitrile and 2.1% selectivity to HCN. It makes operation possible at the relatively low temperature of 320°C with a contact time of 2–5 seconds. It is interesting that this catalyst contains neither bismuth, nor molybdenum nor phosphorus. Still another catalyst that requires a higher temperature of 420°C comprises iron, antimony, molybdenum, vanadium, tellurium, and copper, supported on silica. It gives an overall acrylonitrile yield of 85% and a hydrogen cyanide yield of 3% with no acetonitrile. The ammoxidation reaction is highly exothermic and is carried out in a fluidized bed to ensure effective heat exchange and temperature control.

The fact that the methyl group of propylene can be oxidized preferentially to give acrolein indicates that not all the hydrogens of propylene are equivalent. The methyl hydrogens are allylic and hence reactive; the allyl radical $\text{CH}_2\text{---CH---CH}_2$, on the other hand, is relatively stable. It is the recognition of this difference that makes the oxidation and ammoxidation processes feasible. The stability of the allyl radical is worth illustrating. The heat of the reaction of $\text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{C}_3\text{H}_7 + 0.5\text{H}_2$ is 192 or 177 kJ/mol depending on whether the *n*-propyl or isopropyl radical is formed, whereas the heat of $\text{CH}_3\text{CH=CH}_2 \rightarrow \text{CH}_2\text{---CH---CH}_2 + 0.5\text{H}_2$ is 149 kJ/mol, so that the allyl radical is stabilized to the extent of about 42 kJ/mol.

The mechanism for the formation of acrylonitrile from propylene is similar to the one previously proposed for acrolein formation (Fig. 6.7) and is shown in Figure 6.8. The mechanism is illustrated for the original SOHIO catalyst, an oxidized bismuth molybdenum species, which reacts with ammonia to give the imminium compound (II). This bonds with an allyl radical resulting from the abstraction of a hydrogen from propylene (III) to give (IV). As indicated in (V) a double hydride shift occurs to liberate a mol of ammonia and to give the species (VI). This is oxidized to give (VII), which forms (VIII) by a hydride shift. Compound (VIII) undergoes the transformation shown in (IX) to give the desired product, acrylonitrile, and the catalyst species (X), which with oxygen regenerates the initial catalyst species (I). In the early years of the process, there was the problem of disposal of the acetonitrile and highly toxic hydrogen cyanide by-product, used by the Germans in their death camps.

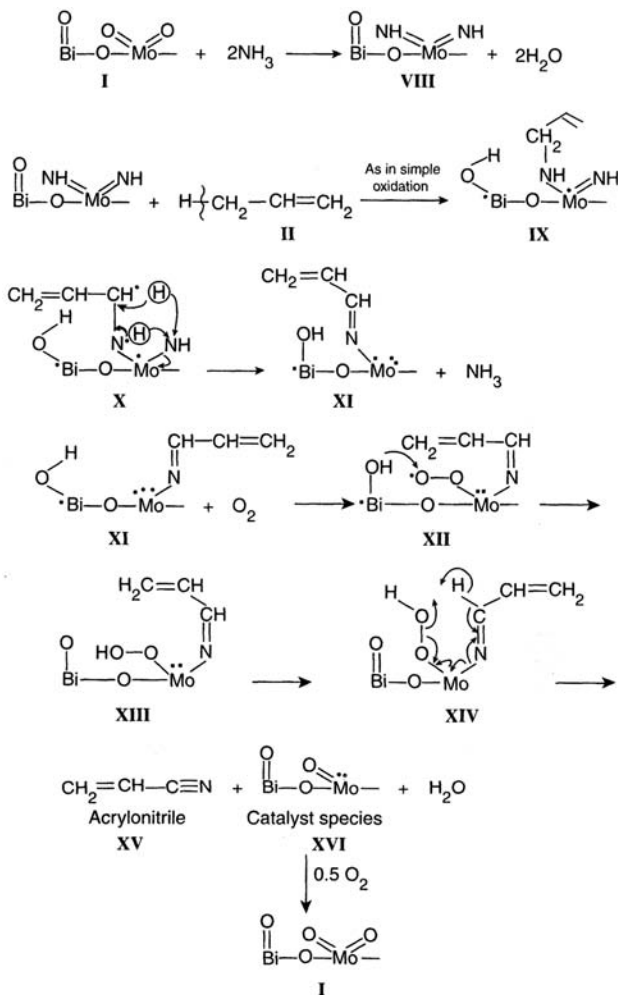
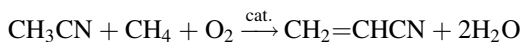


FIGURE 6.8 Mechanism of acrylonitrile formation.

Hydrogen cyanide is used in the major process for methyl methacrylate synthesis (Section 6.7.1), by DuPont for hexamethylenediamine (Section 7.1.5) and for other products such as amino acids (DL-methionine) and chelating agents, but only small uses were found for the acetonitrile. One suggestion was reaction with acetonitrile to give acrylonitrile:



The catalyst comprises potassium or calcium halides on quartz. Molybdenum and bismuth oxides individually or combined on quartz or other supports are also

proposed. The process was never commercialized because the amount of acetonitrile by-product was reduced by catalyst development.

Some acetonitrile is used as an aprotic solvent, particularly for the separation of butadiene from other C₄ olefins (Chapter 7). Modern catalysts are so efficient in decreasing acetonitrile production that, in the early 1990s, there was actually a shortage of acetonitrile for this use. The same situation arose in 2008 and 2009 because of a downturn in the acrylonitrile business. Producers began intentionally to increase yields of by-product acetonitrile, either by raising the temperature, using degraded catalyst, or even injecting ethanol or acetic acid into the reactor.

For many years BP had indicated that its next world scale acrylonitrile plant might be propane based.¹² However, commercialization of this new technology was delayed because of global overcapacity for acrylonitrile in the early 2000s. Finally in 2007, Asahi Kasei announced start-up of the world's first propane-based acrylonitrile plant in Korea. This is a 70,000 metric ton per year line that was retrofitted onto an existing propylene-based acrylonitrile plant.

6.5.1 Uses of Acrylonitrile

Acrylonitrile is used primarily to make polymers. Its most important application is for the production of polyacrylonitrile for textile fibers. Because polyacrylonitrile is not thermally stable, it must be spun from solution just as cellulose acetate is. The problem is that acrylonitrile polymerizes to a very high molecular weight, hence the polymer is only slightly soluble in ordinary solvents, despite the fact that it is thermoplastic. Spinning was made possible by the discovery of so-called aprotic solvents such as *N,N*-dimethylformamide and *N,N*-dimethylacetamide. Polyacrylonitrile is also soluble in aqueous solutions of inorganic salts and acids such as sodium thiocyanate solution and, to a lesser degree, nitric acid and zinc chloride. These are used competitively with the aprotic solvents. The problem of spinning polyacrylonitrile thus gave rise to the science of aprotic solvents, which find application today in extractive distillation (see Fig. 7.2) and in the synthesis of aromatic polymers whose monomers are insoluble in the usual solvents.

Acrylic fibers are also made more tractable by inclusion of 10–15% of comonomers such as methyl acrylate or vinyl acetate. *para*-Vinylbenzenesulfonic acid is also incorporated into the copolymer to make the fiber dyable with basic dyes. Familiar trade names of acrylic fiber are Orlon, Acrilan, and Courtelle.

Another important copolymer made from acrylonitrile is acrylonitrile–butadiene–styrene resin (ABS) (Section 7.1.4). ABS is the most widely used engineering (i.e., metal-replacing) plastic, and global consumption in 2009 was estimated at 6.1 million metric tons. It is a two-phase polymer system, with the elastomeric butadiene–acrylonitrile copolymer dispersed in a rigid styrene–acrylonitrile matrix. Because light reflects at the phase boundaries, it is opaque. Butadiene–acrylonitrile rubber was developed in Germany prior to World War II. It was called Buna N and is still used today. The acrylonitrile imparts valuable oil and abrasion resistance.

High acrylonitrile-containing polymers have good barrier properties to carbon dioxide and oxygen. They are clear and have good extensibility, which makes them

useful for the fabrication of bottles. Monsanto developed such a resin based on a copolymer of acrylonitrile and styrene. The development was banned from food packaging by the Food and Drug Administration because of the slight possibility that some undetectable levels of free acrylonitrile might remain in the resin. This was proved to be unlikely, but Monsanto never reestablished the project and the market for bottles for carbonated beverages was taken over by poly(ethylene terephthalate) (Section 11.3.3). Styrene–acrylonitrile remains a useful copolymer but sells only relatively small volumes. Other acrylonitrile formulations contain styrene, methyl methacrylate, and styrene–butadiene rubber. Barrier resins based on acrylonitrile were available for non-food packaging and were approved for food use in the early 2000s.

The electrohydrodimerization of acrylonitrile provides a significant route to adiponitrile, which in turn can be hydrogenated to hexamethylenediamine for nylon 66 production.¹³ Its economics are less favorable than hydrocyanation of butadiene (Section 5.1.2). What is presumed to be a catalytic route for the dimerization of acrylonitrile was developed by ICI and was scheduled for commercialization in the early 1990s, but ICI instead left the nylon business.

Acrylonitrile production grew slowly in the period 1980 to 1990, at which time acrylic fibers made up 58% of its global market. Fashion trends, however, depressed the market for acrylic fibers and, by 2009, their share of the market had dropped to 40%. Consumption has only been maintained by growth in ABS resins, hexamethylenediamine and acrylamide. Global acrylonitrile demand in 2009 was estimated at 4.9 million metric tons.

6.6 CUMENE/PHENOL AND CUMENE HYDROPEROXIDE

Cumene (isopropylbenzene) is the precursor of phenol and acetone.¹⁴ It results from the acid-catalyzed alkylation of benzene with propylene as shown in Figure 6.4g. It is a continuous reaction similar to ethylbenzene production (Section 5.4) where benzene is alkylated with ethylene. Both liquid and gas phase alkylations are possible. Almost any Friedel–Crafts catalyst can be used. The conventional process, gas phase alkylation, is still the most popular, with aluminum chloride, phosphoric acid, or boron trifluoride catalyst at 200–350°C and 10–15 bar. The molar ratio of benzene to propylene is 8–10:1. Either chemical grade (92 wt%) or refinery grade propylene is suitable. Refinery grade propylene from catalytic cracking is typically about 70% by weight (Section 4.6) with the remainder mostly propane. Cumene yields are 96–97% based on benzene and 91–92% based on propylene. Selectivity to cumene is 92–94% based on propylene, and an excess of benzene is used to depress the formation of di- and tri-isopropylbenzenes as well as a small amount of *n*-propylbenzene.

Solid acid catalysts, such as zeolite ZSM-5, which are more ecologically acceptable, were introduced in the early 1990s and their use has grown rapidly. They offer several advantages over phosphoric acid or aluminum chloride. They are able to bring about the alkylation at lower temperatures and pressures, and reduce the formation of polyalkylbenzenes and olefin oligomers, thus providing overall yields of 98%. In addition, the higher selectivity allows the ratio of benzene to propylene to be

reduced from 8–10:1 to 4–5:1. This doubles the capacity of an existing cumene reactor with virtually no additional capital expenditure, although downstream separation capacity inevitably must be increased. In addition to the savings on operating and capital costs, zeolite catalysts can be regenerated by the burning off of deposits of high molecular weight hydrocarbons. This eliminates the disposal problems associated with phosphoric acid and aluminum chloride. The cumene processes may also incorporate a transalkylation reactor to convert any di- and tri-isopropylbenzene to cumene by reaction with benzene.

Alkylation of benzene with propylene to give cumene was first carried out in refinery polygas units (Section 4.9). Cumene was an important octane improver in aviation gasoline in World War II (Section 4.9). Its production was fostered because polygas units became available when that product was replaced by alkylate (Section 4.10). Conversely, oligomerization can be carried out in units built specifically for cumene production, but seldom is.

Virtually all cumene is converted to phenol and acetone. This is the classic two-for-one reaction in which two products are manufactured in one plant. Cumene is thus the basis for an extensive value chain shown in Figure 6.9. Phenol will be discussed in detail in Section 9.1.

Cumene reacts with oxygen from the air in the presence of aqueous alkali at 130°C and a pH of 6–8 to give cumene hydroperoxide at a concentration of about 25 wt%. An emulsifying agent is often added to facilitate contact between the cumene and aqueous phases. Sodium carbonate is added to maintain the pH. Metallic catalysts such as cobalt, copper, or manganese with promoters may be used, but usually are not, because they facilitate oxidation of the cumene itself to carbon dioxide.

As might be expected, the reaction is sensitive to acids such as formic and acetic, which decompose the cumene hydroperoxide. These are only slowly neutralized by

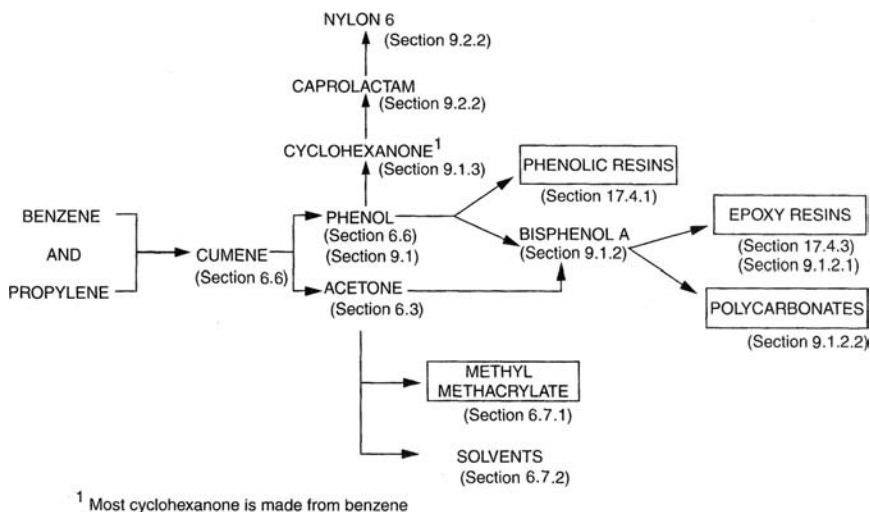


FIGURE 6.9 The cumene value chain.

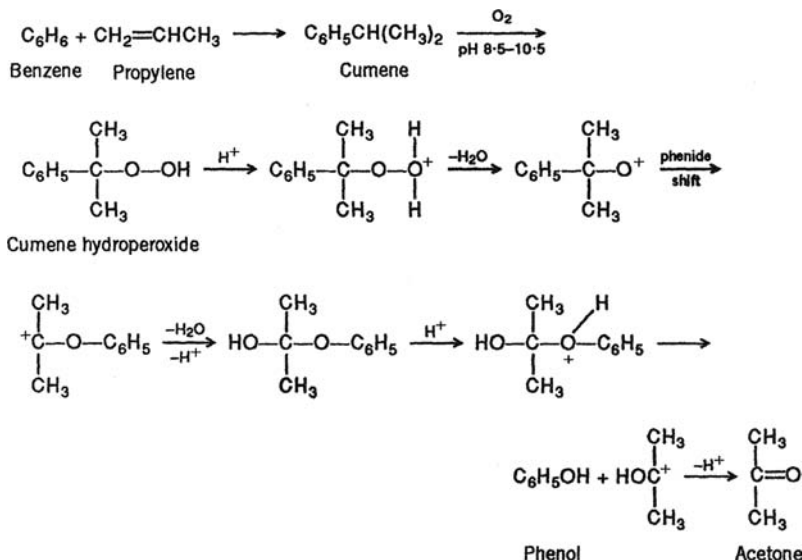


FIGURE 6.10 Mechanism of the cumene–phenol process.

the alkali present, which is in the aqueous rather than the organic phase, but they are also volatilized in the oxygen stream. Other possible impurities in the cumene such as sulfur compounds, phenol, or aniline may also attack the hydroperoxide.

Surplus cumene is distilled off for recycle. The concentrated cumene hydroperoxide (75–85 wt%) is cleaved to phenol and acetone without further purification by treatment with 10% sulfuric acid at about 50°C in the liquid phase. The mechanism for the decomposition is shown in Figure 6.10. By-products are dimethylphenylcarbinol, α -methylstyrene, and acetophenone, as well as diacetone alcohol, which form from the self-condensation of acetone. The stoichiometry demands that 0.6 ton of acetone form for every ton of phenol. The α -methylstyrene in principle is hydrogenated back to cumene and recycled, but the original Distillers cumene–phenol plant at Hull, England, produced negligible amounts of it.

In 2003, Sumitomo Chemical commercialized a new process for making propylene oxide based on oxidation of propylene with cumene hydroperoxide.¹⁵ The cumyl alcohol (dimethylbenzyl alcohol) by-product undergoes dehydration and hydrogenation in one or two steps to reconstitute the starting cumene. This approach to propylene oxide is much less capital intensive than the propylene oxide/styrene monomer or propylene oxide/*tert*-butanol coproduct processes (Section 6.8).

6.7 ACETONE AND ISOPROPANOL

The cumene/phenol process is the major source of acetone. This two-for-one reaction suffers from the same problem as all such reactions in that it is seldom that the marketplace requires both products in the ratio in which they are produced.

Historically, there has been a shortfall of acetone, and it would have been uneconomic to satisfy acetone demand by the accumulation of unsaleable phenol. Hence an alternative route to acetone was required.

The alternative route already existed. It was the first petrochemical reaction, having been pioneered by Exxon, and is shown in Figure 6.4h. Absorption of propylene in concentrated sulfuric acid gave isopropyl sulfate, which was hydrolyzed to isopropanol. This had a number of uses, primarily as a solvent, but some of it was air-oxidized or dehydrogenated to acetone.



The dehydrogenation process was preferred and employed a zinc oxide catalyst at 300–400°C and 3 bar or a copper or brass catalyst at 500°C. Conversions per pass were over 90% and an overall yield of 96% resulted. The oxidative dehydrogenation took place in the presence of air at 400–600°C over a silver or copper catalyst. Low pressures, a temperature of 550°C, and a zinc oxide catalyst were employed. The dehydrogenation was endothermic, and lack of a use for the by-product hydrogen in a plant may have made the oxidative route, which is exothermic, worthwhile.

During the 1980s, acetone from isopropanol accounted on average for about 8% of acetone production in the United States. By 1990 this had fallen to 4.5%. It disappeared completely in the late 1990s because more phenol was needed for bisphenol A (Section 9.1.2) and polycarbonate resins (Section 9.1.2.2), and less acetone for solvent use. INEOS is the world's largest supplier of acetone and phenol.

Mitsui Chemical has developed a process in which what is now a surplus acetone by-product is hydrogenated to isopropanol. This in turn is dehydrated to propylene for recycle to the cumene alkylation unit. Mitsui has the ability to turn this unit on or off depending on the market conditions for acetone.



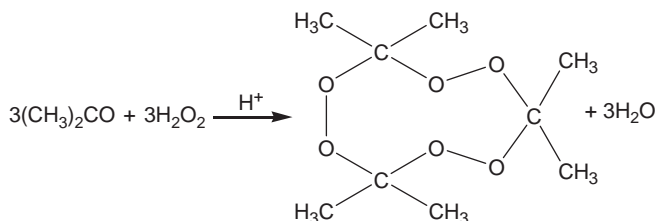
A variant of the Wacker process (Section 5.5) is used in Japan to obtain acetone from propylene. Propylene reacts with oxygen in the presence of catalytic amounts of palladium chloride and a stoichiometric amount of cupric chloride, which is reduced to cuprous chloride. The latter is then reoxidized to cupric chloride in a separate reactor. In the original Wacker process, both the CuCl_2 and PdCl_2 were used in catalytic amounts, the CuCl being reoxidized to CuCl_2 in situ.

A Shell process, not in use, involves the oxidation of isopropanol to acetone and hydrogen peroxide in a two-for-one process.



The three major chemical (i.e., nonsolvent) uses for acetone are for the preparation of methyl methacrylate (Section 6.7.1), methyl isobutyl ketone (Section 6.7.2), and bisphenol A (Section 9.1.2).

When treated with hydrogen peroxide in the presence of a strong acid, acetone gives acetone peroxide, usually as a trimer:



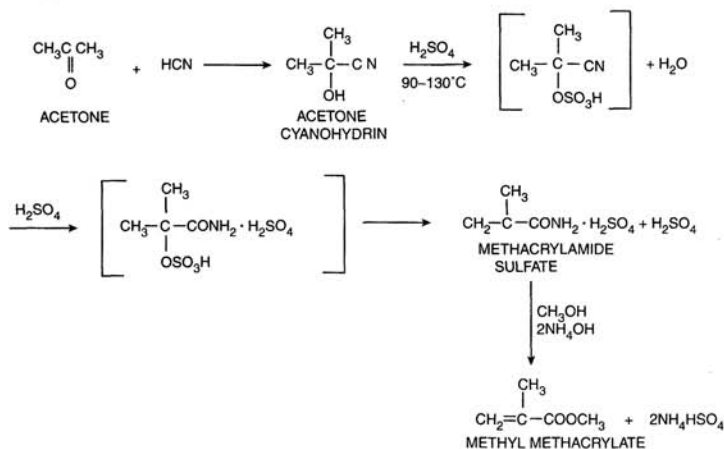
It is a white solid, described on the web and other sources as a high explosive, but it appears to detonate easily when subject to heat, friction, or shock, suggesting that this is a misnomer. It is sometimes formed accidentally, for example, from hydroperoxides in the cumene/phenol process. It is, however, the explosive of choice for terrorists. It is one of the very few explosives not containing nitrogen, which makes it undetectable to nitrogen-sensitive security detectors, and it can be prepared from readily available raw materials.

6.7.1 Methyl Methacrylate

The classical route to methyl methacrylate starts with the sodium hydroxide-catalyzed condensation of acetone and hydrocyanic acid to give acetone cyanohydrin, as shown in Figure 6.11a. Dehydration and hydrolysis of the nitrile group followed by esterification provides methyl methacrylate. The conversion of acetone cyanohydrin to methacrylamide sulfate via acetone cyanohydrin sulfate is carried out with 98% sulfuric acid at temperatures as high as 140°C. The amide reacts with methanol at 80°C to yield methyl methacrylate. Overall molar yield based on acetone has been raised in recent years from 75% to 92%, an indication of the intense process development to which old processes are frequently subjected. The corresponding overall plant yields for methanol and HCN are about 92% and 89%.

A major problem with this process is the production of about 1.5 metric tons of ammonium bisulfate by-product per metric ton of methyl methacrylate by the reactions shown in Figure 6.11a. This by-product problem was never satisfactorily solved over a period of 50 years, but ICI brought a process for by-product treatment on stream in the early 1990s and Mitsubishi Gas Chemical has an entirely new process (see below). Another problem is that about 30% of global hydrogen cyanide production is a by-product from acrylonitrile manufacture (Section 6.5) with the bulk coming from direct on-purpose processes. New acrylonitrile processes generate decreased amounts of hydrogen cyanide, which means that new, dedicated, and for this process uneconomical, hydrogen cyanide facilities (Section 12.1) may be required. These two problems have motivated the development of alternative processes, particularly in Japan, where hydrogen cyanide is in short supply.

(a) CONVENTIONAL ROUTE



(b) MITSUBISHI GAS CHEMICAL ROUTE

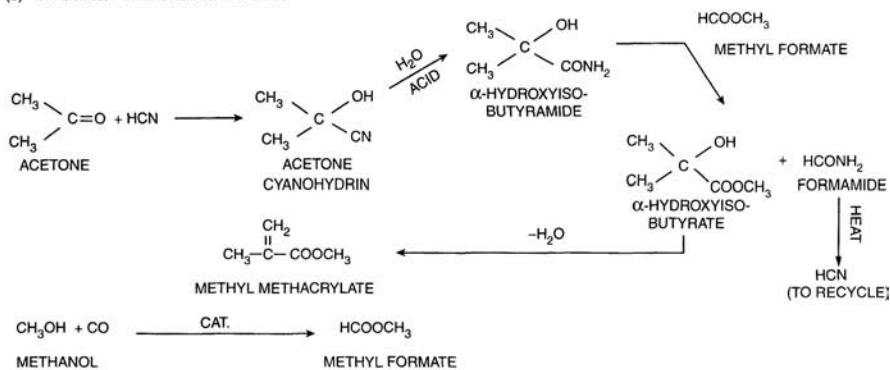
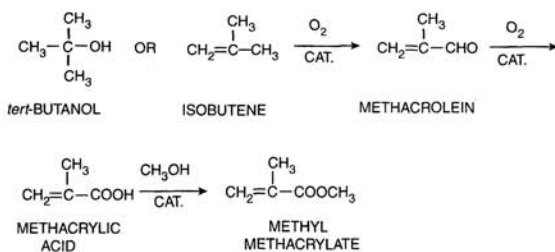
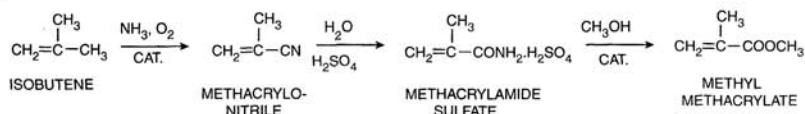
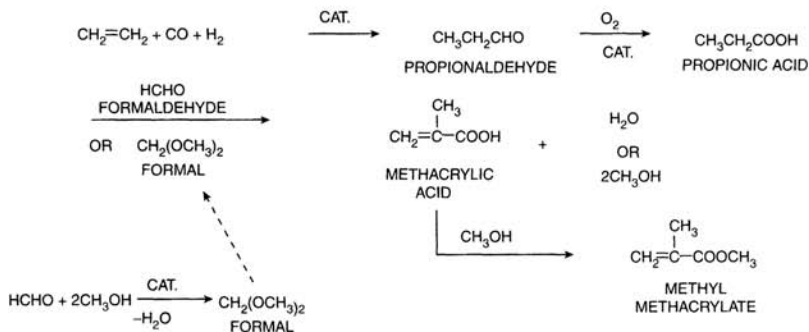
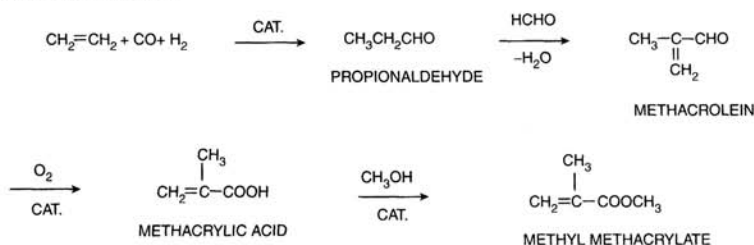
(c) C₄ OXIDATION (SEVERAL JAPANESE COMPANIES)(d) C₄ AMMOXIDATION (ASAHI GLASS CO.)

FIGURE 6.11 Methyl methacrylate syntheses.

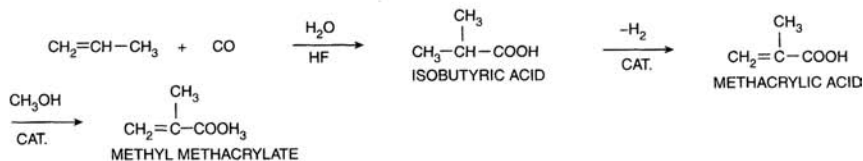
(e) ETHYLENE - BASED (DEVELOPMENTAL, INEOS)



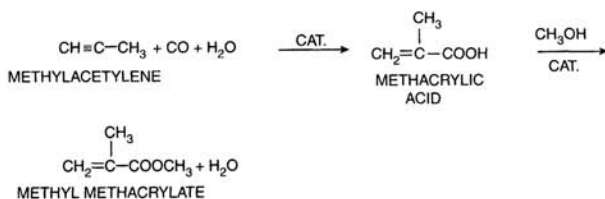
(f) ETHYLENE-BASED (BASF)



(g) PROPYLENE-BASED (DEVELOPMENTAL, ATOCHEM)



(h) METHYLACETYLENE-BASED (DEVELOPMENTAL, SHELL)



(i) ETHYLENE-BASED (ICI/INEOS)

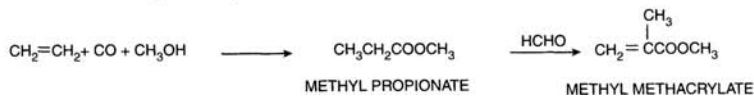
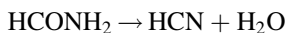


FIGURE 6.11 (Continued)

The ICI process, developed jointly with Air Liquide, is called the “SAROX” process and involves high temperature pyrolysis of the ammonium bisulfate in the presence of air or oxygen. The bisulfate decomposes to ammonia and sulfur trioxide which, at the temperature of operation, dissociates partly to sulfur dioxide and oxygen. The ammonia is oxidized by air to nitrogen and water, and the reaction stream is sent to a sulfuric acid plant where it is reconverted to sulfuric acid, which is recycled. Overall conversion and recovery of the sulfur content of “spent acid” as sulfuric acid is about 90%.

The Mitsubishi Gas Chemical Company process for methyl methacrylate manufacture demonstrates a high level of ingenuity and was announced in 1989. It solves the two defects that characterize the acetone cyanohydrin process – the need to generate hydrocyanic acid and the production of unwanted ammonium bisulfate. It is noteworthy that the solution to these problems did not come from methyl methacrylate’s major suppliers but from a Japanese company.

In this process, acetone cyanohydrin, produced conventionally from acetone and hydrocyanic acid, is partially hydrolyzed to α -hydroxyisobutyramide (Fig. 6.11b). An ester–amide interchange with methyl formate produces methyl α -hydroxyisobutyrate. Thus the carboxyl function has been inserted in the molecule without ammonium bisulfate production. Formamide is the coproduct. Dehydration of the butyrate provides the desired methyl methacrylate. Hydrocyanic acid is regenerated for reuse by dehydrating the formamide:



The dehydration is performed in the gas phase, catalyzed by iron with magnesium, calcium, zinc or manganese promoters at about 400°C, or by α -alumina at 450–540°C at reduced pressure. The need for a dedicated plant for hydrocyanic acid production is thus obviated. Make-up hydrocyanic acid can be generated from formamide made by reacting methyl formate with ammonia. The methyl formate required for this use, as well as for the exchange reaction, is made by the carbonylation of methanol with a basic catalyst. Thus the overall reaction for the MGC process consumes only acetone, methanol, and carbon monoxide, with the CO replacing HCN as the source of the fourth carbon atom needed to convert acetone to methyl methacrylate.

By early 1990, Mitsubishi Gas Chemical Company. was operating a pilot plant for this process and a full scale plant was built in 1997 at Niigata, Japan. Patents granted to MGC reveal some improvements to two of the reaction stages. In particular, instead of the α -hydroxyisobutyramide undergoing an ester–amide interchange with methyl formate, the amide is reacted with methanol with simultaneous removal of the evolved ammonia to give methyl α -isobutyrate (Fig. 6.11b). The other improvement relates to regeneration of HCN. The ammonia by-product is reacted with methanol and oxygen over a ferric/molybdenum oxide catalyst. Thus the overall process converts acetone, methanol, and oxygen to methyl methacrylate.

Unfortunately, this creative process has too many steps, which makes it less economical in the United States than isobutene oxidation. This is especially true because MTBE production has decreased markedly in the United States, making large quantities of isobutene potentially available (Section 7.2.1).

A summary of other processes follows.¹⁶ In the Mitsubishi Rayon Process in use in Japan (Fig. 6.11c) *tert*-butanol or isobutene is oxidized to methacrylic acid, via methacrolein, which is not isolated. If *tert*-butanol is used the reaction probably proceeds via its dehydration to isobutene. Catalysts are similar to those described for the oxidation of propylene to acrolein and acrylic acid (Section 6.4) and are based on molybdenum and bismuth. A typical catalyst for the first stage to methacrolein comprises molybdenum, bismuth, iron, and lithium in a molar ratio of 1:1:0.3:0.1. The second stage of the oxidation may be carried out with a vanadium phosphomolybdate catalyst with cesium and strontium. A typical composition is $\text{Mo}_{12}\text{P}_2\text{VCs}_2\text{SrO}_{0.5}$. Japan Catalytic in a joint venture with Sumitomo oxidizes isobutene directly.

In much the same way that propylene undergoes ammoxidation to acrylonitrile, Asahi Chemical in Japan ammoxidized isobutene to methacrylonitrile in a converted acrylonitrile plant (Fig. 6.11d).¹⁷ Thereafter, the process uses conventional chemistry. This is a multi-stage process and generates ammonium bisulfate in the hydrolysis of the nitrile to the amide. While this approach was apparently economic because it was carried out in depreciated equipment, it was closed down in the late 1990s.

Asahi Chemical has devised a two-step process ("Direct Metha" process) to methyl methacrylate that involves oxidation of isobutene to methacrolein followed by simultaneous oxidation and esterification to methyl methacrylate. The economics appear excellent, and such two-step processes will probably be the major ones in the future. Mitsubishi Rayon announced a similar process in the early 2000s.

A synthesis announced as a commercial process by BASF (Fig. 6.11f) in the late 1980s is based on the hydroformylation of ethylene to propionaldehyde (Sections 5.11.1 and 4.9). Reaction of propionaldehyde with formaldehyde yields methacrolein. Oxidation of the methacrolein gives methacrylic acid which, following esterification with methanol, finally affords methyl methacrylate. Methyl propionate may be used instead of propionaldehyde.

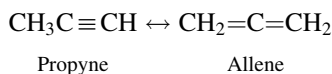
A newer but related process was developed by INEOS, which bought ICI's methacrylate business. Figure 6.11e shows the production of propionic acid, which is then treated with formaldehyde or dimethyl formal to give methacrylic acid. Although the process appears cumbersome, it must be recognized that only the intermediate step of inserting the methylene group, which also was used in a proposed acrylic acid process (Section 6.4), is new. Whereas formaldehyde may be used directly, the dimethyl formal, produced from formaldehyde and methanol, will be more compatible and may lead to higher selectivities. On the other hand, the methanol generated in the condensation must be recovered. In ethylene-based processes, three of the five carbon atoms are derived from syngas, either directly or indirectly, and the economics of this process depends on the economics of syngas production.

Another ICI/INEOS ethylene-based route reacts methyl propionate with formaldehyde to give methyl methacrylate and water.¹⁸ This process is called the Alpha process and is owned by Lucite (and recently acquired by Mitsubishi Rayon). It is based on completely new chemistry, notably the combined carbonylation and esterification of ethylene to methyl propionate. The methyl propionate is reacted with formaldehyde under almost anhydrous conditions to form methyl methacrylate

(Fig. 6.11i). Lucite started up a 120,000 metric ton per year plant in Singapore in 2008, and also announced that the same technology will be used for an even bigger plant (250,000 metric tons) to be built during 2010 and 2011.

A process under development by a number of companies, particularly Atochem, involves propylene carbonylation in the presence of liquid hydrofluoric acid (Fig. 6.11g) to yield isobutyric acid. Oxidative dehydrogenation to methacrylic acid takes place in the presence of aluminum-modified iron phosphate. Esterification with methanol yields methyl methacrylate.

Shell developed a process shown in Figure 6.11h, and sold it to ICI and then to INEOS. It starts with propyne (methylacetylene) or a mixture of propyne with allene $\text{CH}_2=\text{C}=\text{CH}_2$, the latter being in equilibrium with propyne under the reaction conditions:



Propyne and allene are produced during steam cracking (Section 4.5.1) in small quantities and can be recovered by solvent extraction, although they are usually selectively hydrogenated to propylene. Since they are produced in small quantities, isolation of sufficient material to feed a plant could be a problem. In the Shell/INEOS process, however, the mixture is reacted with carbon monoxide and water in the presence of a catalyst comprising palladium acetate, triphenylphosphine, and benzenephosphonic acid. Methacrylic acid results, which is esterified to methyl methacrylate. Alternatively, the carbonylation can be carried out in the presence of methanol rather than water to yield the ester directly. The process is closely related to an obsolete, but at one time a preferred process for acrylic acid production from acetylene, which used a conventional nickel carbonyl catalyst (Section 6.4).

The target of derivatizing alkanes led to yet another route to methyl methacrylate, starting with isobutane. It was actively under investigation in the late 1990s and early 2000s. This approach has the obvious appeal of a low cost feedstock but suffers from the tremendous difficulty of developing catalysts with sufficient selectivity. More about alkane derivitization is described in Chapter 13.

Evonik Industries AG has developed a route to methyl methacrylate that avoids the use of sulfuric acid. Like the traditional acetone cyanohydrin process, the Aveneer[®] process is based on the starting materials hydrogen cyanide (from ammonia and methane, Section 14.1), acetone, and methanol, but without the additional use of sulfuric acid. This not only eliminates the largest feedstock by volume (sulfuric acid), but also eliminates the sulfuric acid recovery section of the plant. The key to the Aveneer process is the combination of purely catalytic processes providing more or less almost complete selectivity at each step. Evonik claims that the energy consumption is about halved and that yields based on acetone as well as on HCN are significantly enhanced compared with the acetone cyanohydrin process. In addition, ammonia can easily be recovered and recycled as a feedstock for HCN. A plant is planned to come on stream in 2014.¹⁹

Another proposed methyl methacrylate process, which yields propylene oxide as a coproduct, is described in Section 4.7. Despite all these interesting new processes, 70% of the world's methyl methacrylate was still produced in 2009 by the acetone cyanohydrin route, in spite of the problems of ammonium bisulfate disposal and hydrogen cyanide safety. In 2007, all the U.S. capacity and all the West European capacity except that of BASF were acetone cyanohydrin based. The global MMA market is highly concentrated, with only a few major producers. Historically there were five top producers, namely, Lucite (formerly ICI), Rohm and Haas, Mitsubishi Rayon, Degussa, and Sumitomo Chemical holding about two-thirds of the market share. However, the industry has changed tremendously during the last few years. RAG acquired Degussa in 2004 and later grouped its chemical business into Evonik Industries. Dow Chemical successfully completed acquisition of Rohm and Haas in March to April 2009. Mitsubishi Rayon completed acquisition of Lucite International, demerged from Evonik in May 2009, making itself the largest MMA producer in the world, with market share of about 30%. Lucite produces MMA in the United States, United Kingdom, China, Taiwan, and Singapore while Mitsubishi Rayon owns plants in Japan, Thailand, and China. Its acquisitions give Mitsubishi capacity in all major regions and it also owns three MMA technologies—ACH, isobutene, and ethylene.

Global consumption of MMA in 2009 was approximately 3.6 million metric tons. Most methyl methacrylate is polymerized to poly(methyl methacrylate) from which is made acrylic sheet for use in glazing, lighting, signs, and sanitary items such as bathtubs made by thermoforming (Fig. 6.12). Glazing, in which the transparent poly

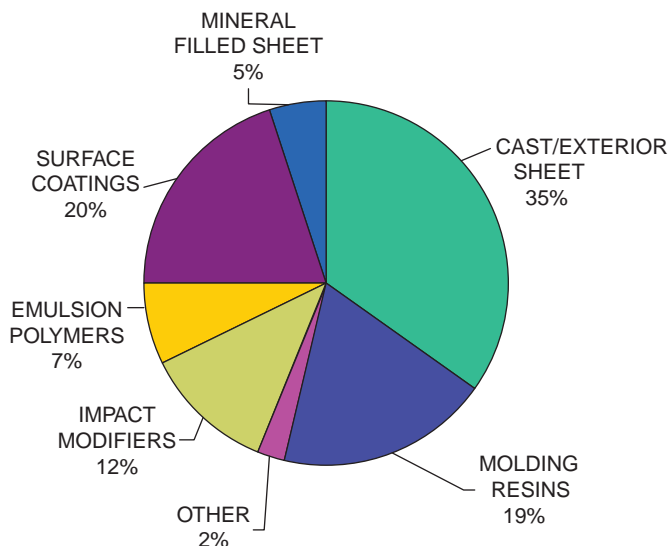


FIGURE 6.12 Western Europe methyl methacrylate demand pattern (2008). (Source: Lucite International.)

(methyl methacrylate) replaces glass, is by far the largest market. Molding resins and surface coatings provide the other two large applications. Methyl methacrylate is used with other acrylic monomers to make emulsions for water-based paint (Sections 6.4 and 5.4). Combined with melamine resin (Section 12.5.1.3) it is the vehicle for the paint used both as the pigmented topcoat for automobiles as well as the clear coat that completes the finish. It also replaces styrene in certain specialty unsaturated polyester compositions (Section 11.1.3). If fears of styrene toxicity in polyester resins turn out to be well founded, methyl methacrylate consumption will increase. Methyl methacrylate has a high refractive index and critical angle and hence is capable of conducting light around bends. This is the basis for its growing use in fiber optics and light pipes. By far the largest emerging application is in liquid crystal display (LCD) extruded sheet applications. The enormous present and potential growth for LCD screens for home theater, flat screen TVs, computer monitors, and so on has been a major driver for methyl methacrylate expansions, especially in Asia where virtually all the LCD market now concentrates.

6.7.2 Methyl Isobutyl Ketone and Other Acetone Derivatives

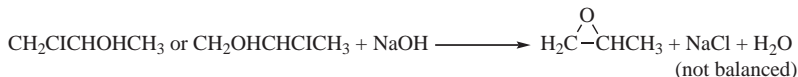
Further products from acetone are shown in Figure 6.13. Practically all the materials are solvents, mostly for the paint industry. The most important, as previously indicated, is methyl isobutyl ketone. The aldol condensation of acetone to diacetone alcohol is base-catalyzed and carried out in the liquid phase. Dehydration takes place at about 100°C in the presence of sulfuric and phosphoric acids to yield mesityl oxide. Hydrogenation of mesityl oxide to methyl isobutyl ketone must be accomplished without involving the carbonyl group. Actually the hydrogenation is carried out with copper and nickel catalysts at 150–200°C and up to 10 bar to give a combination of methyl isobutyl ketone and methyl isobutyl carbinol, which can be separated by distillation.

Isophorone, a high boiling ketone solvent, results from the base-catalyzed trimerization of acetone (Fig. 6.13). Hydrocyanic acid will add across its double bond to give a nitrile, and reductive amination with ammonia and hydrogen gives “isophorone diamine.” Like the toluene diamines, treatment with phosgene gives a diisocyanate, isophorone diisocyanate or IPDI, that is used in a light stable polyurethane resin.

Hydrogenation of isophorone reduces the double bond and converts the ketone group to an alcohol. Nitric acid oxidation provides 2,2,4-trimethyladipic acid, which may be converted to a dinitrile with ammonia. Further hydrogenation yields 2,2,4-trimethylhexamethylenediamine. Both these diamines, but particularly isophorone diamine, are useful as curing agents for epoxy resins.

6.8 PROPYLENE OXIDE

Propylene oxide (Fig. 6.4e, f) was made traditionally by reaction of propylene with hypochlorous acid, generated in situ from chlorine and water, followed by dehydrochlorination with calcium or sodium hydroxide. The route has been known

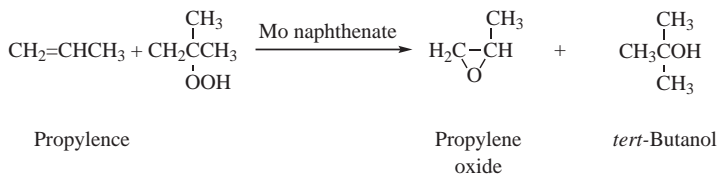
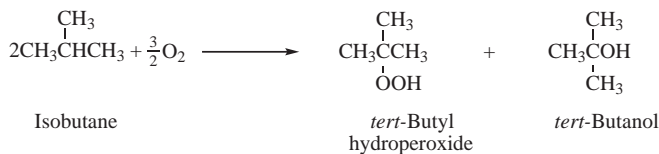

$$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{HCl}$$


The same process was at one time used for ethylene oxide, with calcium hydroxide generally preferred to sodium hydroxide in the final stage. Many of these plants were converted to propylene oxide production when the direct oxidation route (Section 5.7) to ethylene oxide appeared. The process for propylene oxide with sodium hydroxide is still used by Dow in the United States. Several European and Japanese companies use

the calcium hydroxide process. Dow has a highly integrated plant with a chlorine/caustic soda unit to provide chlorine for the chlorohydrin reactor and sodium hydroxide for the dehydrochlorination. In addition, the brine produced by the dehydrochlorination can be reprocessed into caustic and chlorine, although Dow probably does not do this.

The reaction takes place in dilute solution and 4.0–4.5% propylene chlorohydrins (the α -isomer predominates) is produced in a molar yield of 94% with 4.7% of 1,2-dichloropropane and 1.7% of chloroisopropyl ether. In the dehydrochlorination the yield of propylene oxide is 96%.

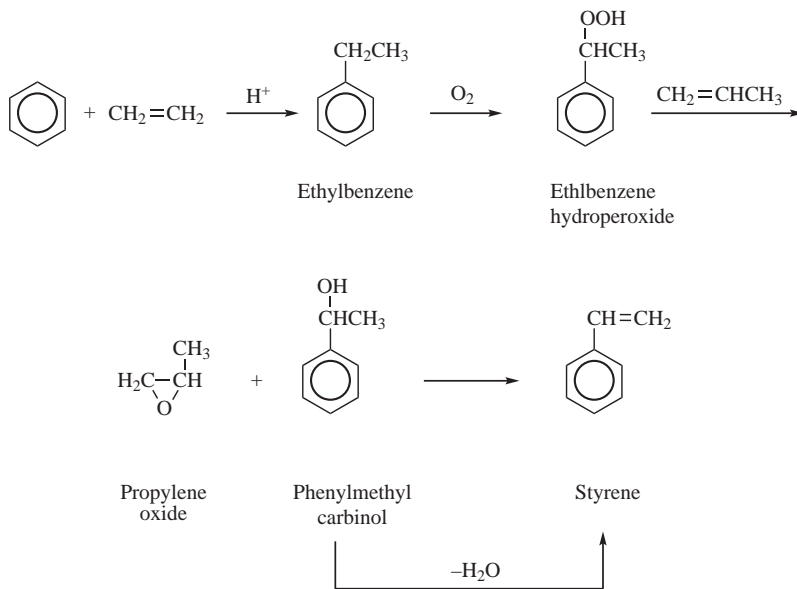
The process is wasteful of chlorine (or electricity in the integrated plant) and much research was devoted to discovering a direct oxidation route.²⁰ The first process to be commercialized involved oxidation of isobutane to *tert*-butyl hydroperoxide, which then oxidized propylene to propylene oxide. Oxirane, a joint venture between Scientific Design and ARCO Chemical, built the first plant using this process in 1969.



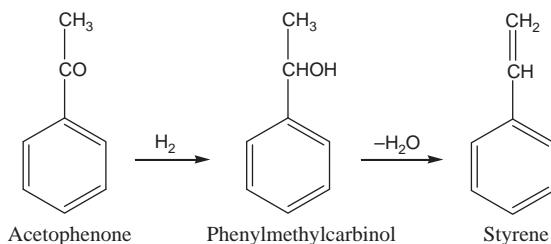
tert-Butanol is a by-product in both the formation of the peroxide and the epoxidation step. Approximately 2.2 mol of *tert*-butanol per mol of propylene oxide is produced. The reaction provides a second route to *tert*-butanol, the first being the in situ hydration of the isobutene in the C₄ fraction from steam or catalytic cracking. This low melting (mp. 25.6°C) white solid can be oxidized to methyl methacrylate as is done in Japan (Section 6.7.1). It aroused interest as an octane improver in nonleaded gasoline, where it may be used in combination with methanol. However, methyl *tert*-butyl ether (Section 7.2.1) was felt at the time to be superior, although this view has now changed. Accordingly, in the late 1980s, ARCO Chemical, who pioneered the two-for-one reaction with Scientific Design for propylene oxide and *tert*-butanol, started to dehydrate *tert*-butanol to isobutene for conversion to methyl *tert*-butyl ether and quickly became the largest single U. S. producer of this gasoline additive.

Pure oxygen is required for the isobutane hydroperoxidation. The uncatalyzed liquid phase reaction proceeds at 120–140°C and 34 bar. Acetone forms as a minor by-product. Water is necessary in the reaction mixture to inhibit oxidation of isobutane to ketones, aldehydes, and acids. The subsequent epoxidation is carried out at 135°C and about 50 bar to keep the reactants in the liquid phase and requires a molybdenum naphthenate catalyst.

Oxirane (now LyondellBasell) developed a second two-for-one process for propylene oxide. It provides styrene as a coproduct and is often termed POSM (propylene oxide/styrene monomer). Between 2.2 and 2.4 kg of styrene is generated for each kg of propylene oxide. Thus the first plant was owned by Repsol (licensed from Oxirane) and started up in 1974. It produced 168,000 metric tons of styrene and 70,000 metric tons of propylene oxide per year. Benzene and ethylene give ethylbenzene, which was converted to ethylbenzene hydroperoxide with air. This epoxidizes propylene to propylene oxide, yielding coproduct phenylmethylcarbinol, whose dehydration provides styrene (Section 5.8).



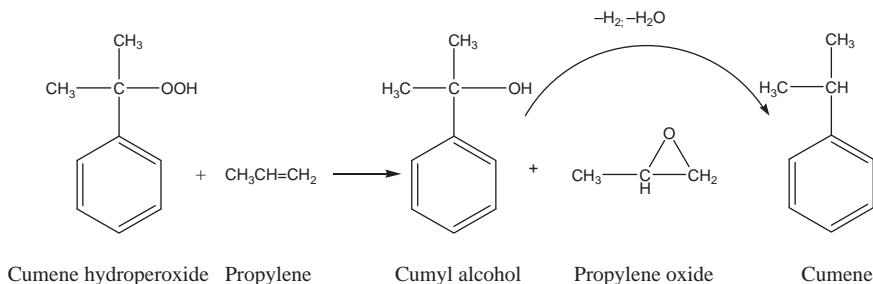
Because of the problems of isolating and recovering styrene, capital investment for this process is about twice as much as that for the propylene oxide/*tert*-butanol process. The process is similar to the oxidation of cumene to cumene hydroperoxide (Section 6.6) and isobutane to *tert*-butyl hydroperoxide. Magnesium carbonate is added to adjust the pH to 7 to reduce the decomposition of the hydroperoxide. Selectivity to about 65% is possible only at a low conversion of 15–17%. Above that concentration, by-products including phenylmethylcarbinol and acetophenone increase appreciably. Meanwhile, acetophenone can be converted to styrene by hydrogenation to phenylmethylcarbinol and subsequent dehydration.



The epoxidation stage is also similar to the production of *tert*-butyl hydroperoxide, a molybdenum naphthenate catalyst playing an important role. However, this requires milder conditions of 100–130°C in the liquid phase under ambient pressure. Selectivity of propylene to propylene oxide is about 91%. By-products include dimers of propylene, whose formation can be inhibited by antioxidants. The vapor phase dehydration of phenylmethylcarbinol to styrene takes place over a catalyst at 200–280°C. Titania and alumina are typical catalysts.

A Shell variation of the Oxirane/LyondellBasell route to propylene oxide and styrene involves a heterogeneous system for the epoxidation, with catalysts such as vanadium, tungsten, molybdenum, or titanium supported on silica and treated with a silylating agent. Five plants using this technology are in operation, two in Europe, one by Shell and one by ELLBA, a joint venture of Shell and BASF; two in Singapore, again one by Shell and one by ELLBA. The newest one is in China, owned by CSPC, a joint venture of Shell and CNOOC. By 2009, 20% of styrene globally was made by the coproduct process.

Before these plants were built, there was a ferocious commercial battle. In 1998, Dow signed a license for POSM technology and, in July 2000, declared its intention of building a world scale plant on the Gulf Coast. Chemical ingenuity and technological advances undermined this objective. In September 2000, Sumitomo Chemical announced a new coproduct-free route to propylene oxide based on cumene hydroperoxide. Cumene hydroperoxide is the precursor of phenol and acetone (Section 6.6), and thus its manufacture and handling are well known. Sumitomo developed a proprietary catalyst that enables cumene hydroperoxide to epoxidize propylene to propylene oxide in excellent yield giving cumyl alcohol (dimethylbenzyl alcohol) as a by-product. The patents give examples that show that cumyl alcohol can undergo simultaneous hydrogenation and dehydration to cumene, which can be recycled to the beginning of the reaction.



In January 2001, Degussa-Hüls announced the development of a route to propylene oxide based on epoxidation of propylene by hydrogen peroxide (HPPO), and in March BASF made a similar announcement.²¹ Such a reaction has great appeal because of its simplicity; the only coproduct is water. Titanium/silicalite is an extraordinarily selective catalyst for this reaction, affording selectivities over 95%. The major by-product is propylene glycol, formed from the reaction of propylene oxide with by-product water. Dow was overwhelmed by the plethora of processes and in April 2001 delayed their POSM plant indefinitely.

To add to the excitement, the Shell magazine for the second quarter of 2001 said that Shell itself was working on direct and cumene hydroperoxide-based routes to propylene oxide.

In August 2002, BASF and Dow formed a joint venture to build a new 300,000 metric ton per year HPPO plant in Antwerp, Belgium, which came on stream in 2008. In August 2003, Sumitomo brought on stream the propylene-oxide-only plant described above. In September 2003, Degussa and Sasol announced plans for an HPPO plant in South Africa.

In the past, the problem with this approach was that hydrogen peroxide (Section 9.8.1) was too expensive. The cost issue was partially solved by Solvay. Solvay developed technology that allows for “megascale” hydrogen peroxide plants that will reduce the cost of hydrogen peroxide manufacture and hence improve the economics of HPPO routes. Details of the process are sparse, but a Solvay presentation²² implies that they are using a modification of the longstanding process based on ethylan-thraquinone or, at any rate, a cyclic process involving a quinone. A possible process involving only hydrogen and oxygen is at the research stage (Section 9.8). Solvay built a megascale hydrogen peroxide plant next to the BASF/Dow HPPO plant in Antwerp. They have devised a new “high-productivity/high-yield” process, based on an optimized distribution of isomers of 2-amyl anthraquinone.²³ In 2008, they built a “megascale” single-train plant in Zandvliet, near Antwerp (Belgium). The plant has an annual production capacity of 230,000 metric tons per year, more than twice that of the world’s next-largest single-train plant. It is owned 50% by Solvay and 50% by BASF/Dow. Independently, Degussa (Evonik) has developed and is licensing its own version of HPPO. The first Degussa technology-based plant, with a capacity of 100,000 metric tons/year, was built by SK Chemicals and started up in 2008 in Ulsan, South Korea. An even larger plant is scheduled to come on stream at Map Ta Phut (Thailand) in 2011. It is likely that this will reduce the cost of hydrogen peroxide manufacture and hence improve the economics of HPPO routes.

By 2009, when the dust had largely cleared, 46% of propylene oxide production was still made by the chlorohydrin method. This is doubtless the contribution of the huge Dow plant. Thirty percent was made by POSM, 16% by the *tert*-butanol coproduct process, and the remaining 8% by the new coproduct-free processes.

6.8.1 Other Propylene Oxide Processes

Much work has been done over the years on other options for production of propylene oxide and the corresponding glycol. Some of which do not generate coproducts. Processes developed to various degrees include:

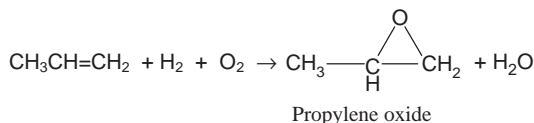
1. Acetoxylation of propylene
2. Direct oxidation
3. Use of peracids
4. Electrochemical processes
5. Biotechnological approaches

6.8.1.2 Direct Oxidation

A key difference between ethylene and propylene is the fact that propylene contains “allylic hydrogens” that are sensitive to oxidation; hence the success of such propylene oxidation processes as acrylic acid and acrylonitrile. Ethylene, having no allylic hydrogens, undergoes silver-catalyzed epoxidation with oxygen fairly robustly (>80% selectivity). In contrast, the analogous direct oxidation of propylene has not proved commercially feasible. Propylene reacts with oxygen in the presence of silver with low selectivity to give numerous by-products together with carbon dioxide and water from combustion processes.

Typical of work in this area is that of Union Carbide, now Dow Chemical, and Phillips which have developed noncatalytic liquid phase acetoxylation processes in organic solvents such as acetonitrile and methyl formate at 150–225°C and 5–14 bar. Selectivities of 55–65% were achieved at propylene conversions of less than 25%. Work in the late 1990s by ARCO Chemical with silver catalysts has shown selectivities up to 59% to propylene glycol mono- and diacetates at propylene conversions of 4.5%. However, in order to achieve this relatively high selectivity, low pressures and accordingly low throughputs were necessary.

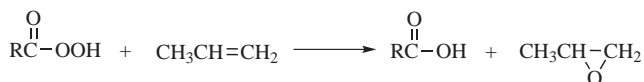
A related approach is to react propylene with a mixture of oxygen and hydrogen gas over gold and titanium catalysts. Use of mixtures of oxygen and hydrogen to epoxidize propylene is termed hydro-oxidation. Nippon Shokubai, LyondellBasell, and Dow Chemical are active in this area; indeed in 2002, Lyondell announced construction of a pilot plant for the direct oxidation of propylene to propylene oxide.



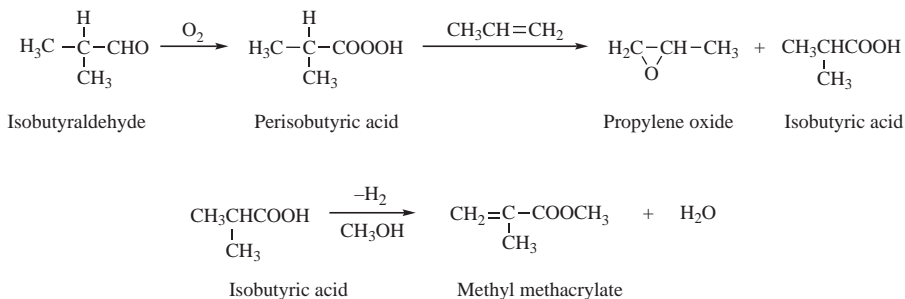
It is likely that this reaction proceeds through some sort of peroxy intermediate. While patents indicate that high selectivities are possible, conversions per pass are less than 3% at best and typically often less than 1%, far too low for commercial exploitation.

6.8.1.3 Use of Peracids

The use of peracids provides an elegant way of transferring oxygen to the double bond of propylene. The peracid is converted correspondingly to the parent carboxylic acid.

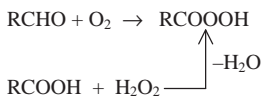


These processes are related to the previously described hydroperoxide processes. A process involving the coproduction of propylene oxide and methyl methacrylate has been suggested. It starts with isobutyraldehyde, which is converted to perisobutyric acid. This in turn oxidizes propylene to propylene oxide and gives isobutyric acid, which can be esterified and dehydrogenated to methyl methacrylate.

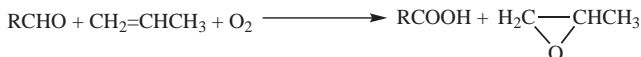


Isobutyric acid is an intermediate in one of the propylene-based routes to methyl methacrylate (Section 6.7.1). Isobutyraldehyde is an undesired by-product in the cobalt-catalyzed hydroformylation of propylenes (Section 6.9). Lack of demand, except from Eastman and BASF, which convert it to neopentyl glycol (Section 6.9.1), motivated the development of the elegant rhodium-based catalyst system that provides high yields of *n*-butyraldehyde.

In addition to perisobutyric acid, the peracids of formic, acetic, and propionic acids can be used to make propylene oxide. The peracid can be prepared either by oxidizing the corresponding aldehyde or by reacting the corresponding carboxylic acid with hydrogen peroxide.



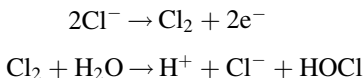
In a single-step process, the percarboxylic acid is formed *in situ* by the oxidation of the aldehyde in the presence of propylene. The percarboxylic acid that forms epoxidizes the propylene immediately. In a two-step process, the percarboxylic acid is isolated and used to epoxidize propylene in a second step.

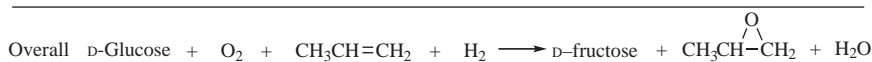
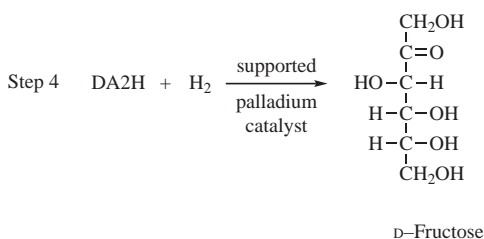
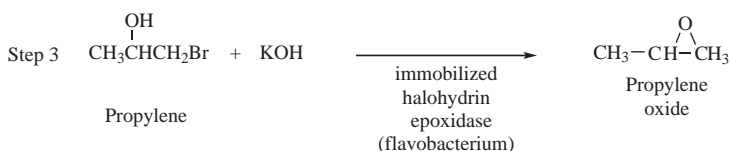
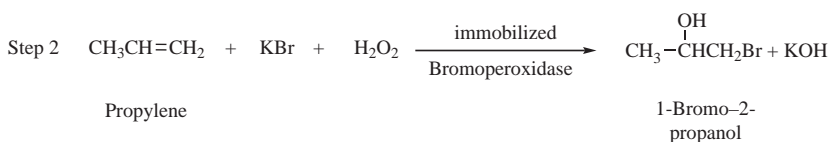


Although results are excellent, the processes have said not to be economic because of the high cost of hydrogen peroxide. If the peracid is prepared from an aldehyde, economics are better but not on a par with the previously described hydroperoxide processes. Solvay's building of huge new hydrogen peroxide plants in connection with HPPO technology (Section 6.8) should have altered this, but there appear to be no new initiatives.

6.8.1.4 Electrochemical Processes

The electrochemical processes suffer from high energy cost. Typically, brine is electrolyzed in the presence of propylene. The overall reaction is simple, although many reactions are involved. At the anode, chloride ions are discharged to give chlorine, which reacts with water to form hypochlorous acid.



$$\begin{array}{ccc}
 \text{Step 1} & & \\
 \begin{array}{c} \text{CHO} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{OH}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array} + \text{O}_2 & \xrightarrow[\text{glucose-2-oxidase}]{\text{immobilized}} & \begin{array}{c} \text{CHO} \\ | \\ \text{C}=\text{O} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array} + \text{H}_2\text{O}_2 \\
 \text{D-Glucose} & & \text{D-Arabinose-2-hexosulose (DA2H)}
 \end{array}$$


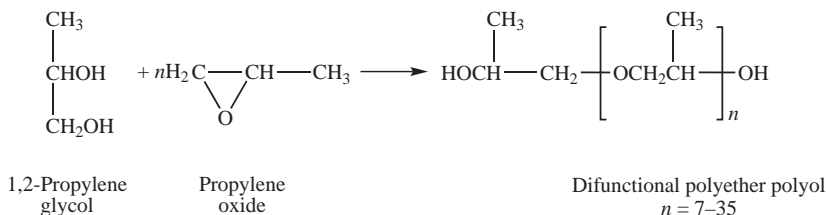
The key to this imaginative process was the discovery of a peroxidase that forms the bromohydrin.

An Exxon process is based on a microorganism, which consumes methane and can oxidize propylene to propylene oxide. Methylophilic organisms, however, can only function with a coenzyme that undergoes a redox cycle with a readily oxidizable material such as methanol that oxidizes to formaldehyde. The fragile enzyme and coenzyme are resident in a monocellular microorganism, and the cell rather than the enzymes can be used. Even so, the scale-up of such a process presents formidable problems.

These ingenious but currently uncommercialized processes are described to emphasize that choice of R&D projects is one of the serious problems facing chemical companies today. It has always been a problem, but viability of projects was more obvious in the 1950s and 1960s than in the 1990s and 2000s. The search for the “no-go” factor and the attempt to resolve it before expensive development is undertaken are keys to any project evaluation. As modern biotechnology becomes more and more sophisticated, these currently “impractical” processes may well presage the future.

6.8.2 Propylene Oxide Applications

Whereas 60% of ethylene oxide is hydrolyzed to ethylene glycol, only about one-fifth of the propylene oxide produced is converted to propylene glycol. The major use, and the reason for the increased consumption of propylene oxide in the past 35 years, is its oligomerization to poly(propylene glycols), otherwise known as polyether polyols, for polyurethanes (Sections 9.3.1 and 10.3). They account for 60% of production. The oligomerization is initiated by active hydrogen compounds. To provide the hydroxyl end groups necessary for interaction with isocyanates, propylene glycol may be used as the initiator.



The polymerization proceeds head-to-tail to give mainly secondary hydroxyl end groups. The polyols and polyethers react with diisocyanates, especially MDI, PMDI, or toluene diisocyanate (Sections 9.3.1 and 10.3), to give polyurethane resins. If a more highly crosslinked polymer is desired, as is frequently the case, a triol can be prepared by the interaction of glycerol or trimethylolpropane with 3 mol of propylene oxide. If more active hydroxyl groups are required, reaction with ethylene oxide provides primary hydroxyethyl groups.

The second largest application of propylene oxide is its reaction with water to give 1,2-propylene glycol.

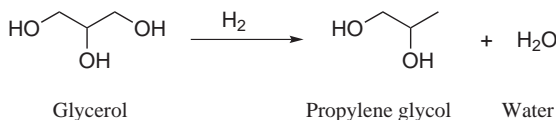


In practice, a large excess of water is used to inhibit the formation of oligomers. If the amount of water is decreased, dipropylene and tripropylene glycols form and indeed poly(propylene glycols) with molecular weights of several thousands can be made. Because propylene glycol, unlike ethylene glycol, is not toxic it can be used in cosmetics. The largest use, however, is in the manufacture of unsaturated polyesters (Section 11.1.3). The poly(propylene glycols) can also be manufactured by reacting propylene oxide with propylene glycol. Copolymers of ethylene oxide and propylene oxide are nonionic surfactants.

A potential alternative source of propylene glycol is from the surplus glycerol generated by the production of biodiesel. Typically, 1 kg of coproduct glycerol is produced per 10 kg of biodiesel (fatty acid methyl ester, FAME) from the methanolysis of used cooking oil, plant triglycerides, and soon. While biodiesel production will remain small relative to global diesel fuel demand (projected to be still less than 1.5% in 2015), there will still be large quantities of crude glycerol available. This availability, coupled with a resulting low price for glycerol (particularly crude material), makes it an attractive feedstock for a variety of derivative chemicals – in particular, propylene glycol.

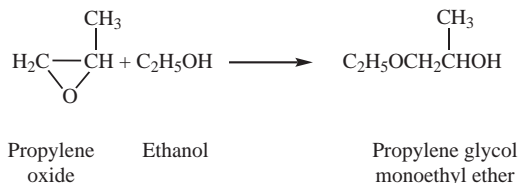
Davy Process Technology (DPT) has developed a gas phase process for the hydrogenolysis of glycerol to propylene glycol. In July 2007 they announced the first license of this process to a joint venture between Cargill and Ashland. The new plant is expected to have an annual capacity of 65,000 metric tons and to be built in Europe. Cargill/Ashland expect the purity of the propylene glycol to be adequate for virtually any propylene glycol application.

The idealized chemistry of this conversion is shown below:



Other companies active in similar areas include Archer Daniels Midland, UOP, Huntsman, Dow, and smaller start-up companies such as Virent and Senergy.

Useful solvents result when propylene oxide reacts with alcohols to form glycol ethers.



This is analogous to the reaction of ethylene oxide with alcohols (Section 5.11.6.2). The significant propylene glycol ethers and esters are shown in Table 6.3. The first three are longstanding products, but the remaining four were only toxicologically approved at the turn of the century.²⁴ To some extent they are replacing the ethylene

TABLE 6.3 Propylene Glycol Ethers and Esters

Trivial Name	Chemical Name	Boiling Point	Formula
Propylene glycol methyl ether (PM)	1-Methoxypropan-2-ol	120	$\text{CH}_3\text{OCH}_2\text{CHOHCH}_3$
Propylene glycol methyl ether acetate (PMA)	2-Methoxy-1-methylethyl acetate	145.8	$\text{CH}_3\text{OCH}_2(\text{CH}_3)\text{-O-COCH}_3$
Dipropylene glycol methyl ether (DPM)	2-Methoxymethylethoxy propanol	184–197	$\text{CH}_3\text{O}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_2\text{H}$
Propylene glycol <i>n</i> -butyl ether (PnB)	1-Butoxypropan-2-ol	171	$\text{C}_4\text{H}_9\text{OCH}_2\text{CH}(\text{CH}_3)\text{OH}$
Dipropylene glycol <i>n</i> -butyl ether (DPnB)	1-(2-Butoxy-1-methylethoxy)propan-2-ol	230	$\text{C}_4\text{H}_9\text{O}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_2\text{H}$
Dipropylene glycol methyl ether acetate (DPMA)	1(or 2)-(2-Methoxymethylethoxy)propanol, acetate	209	$\text{CH}_3\text{O}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_2\{\text{C=OCH}_3\}$
Tripropylene glycol methyl ether (TPM)	[2-(2-Methoxymethylethoxy)-methylethoxy]propanol	243	$\text{CH}_3\text{O}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_3\text{H}$

oxide-based products, some of which are toxic to humans (Section 5.11.6.2) and hence environmentally undesirable. Because the propylene oxide-based glycol ethers have methyl side chains, they are probably not as good solvents as the ethylene oxide-based products. Even so, increased demand is expected as the corresponding ethylene oxide-based products are phased out. In 2009 they accounted for 11% of propylene oxide consumption. Production of glycol ethers based on propylene oxide in the United States was less than 100,000 metric tons, and in Western Europe about 250,000 metric tons. China consumed about 50,000 metric tons but is expected to be the fastest-growing market. A unique route for producing 1,4-butanediol from propylene oxide was developed by ARCO Chemical (now LyondellBasell). This technology is described in Section 12.3.1.

6.9 *n*-BUTYRALDEHYDE AND ISOBUTYRALDEHYDE

n-Butyraldehyde was originally prepared by the aldol condensation of two molecules of acetaldehyde to yield acetaldol and then crotonaldehyde by dehydration. Hydrogenation of crotonaldehyde provided a mixture of *n*-butyraldehyde and *n*-butanol in a ratio of 70:30 (Section 5.11.3).

The route has been replaced by reaction of propylene (Fig. 6.4i) with carbon monoxide and hydrogen (Section 12.4) at 130–175°C and 250 bar over a cobalt

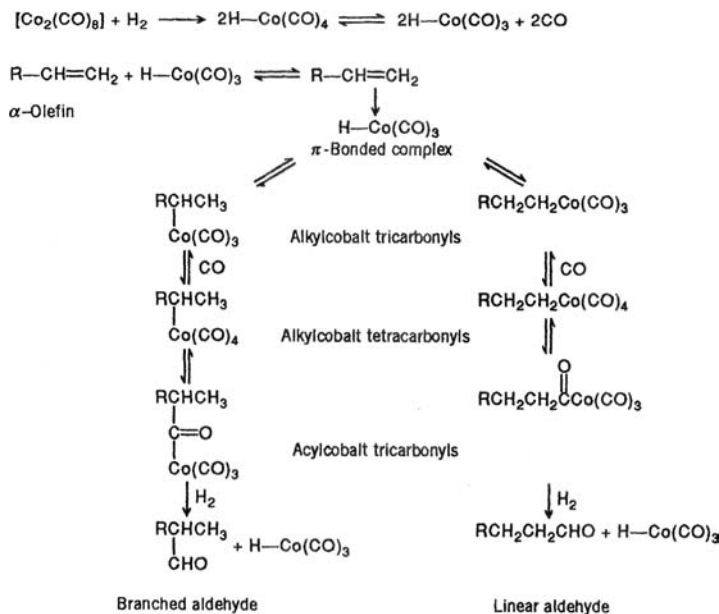


FIGURE 6.14 Hydroformylation–olefin insertion.

carbonyl catalyst to give a mixture of between 3 and 4 mol of *n*-butyraldehyde to 1 mol of isobutyraldehyde. This reaction is called the oxo process or hydroformylation and was invented during World War II by Otto Roelen at Ruhrchemie. The mechanism is shown in Figure 6.14. The cobalt interacts with the olefin to give a π -bonded complex after which there is a rearrangement in which the propylene inserts itself into the Co–H bond. The manner of the insertion determines whether the final compound will be linear or branched. The two possibilities are shown in the figure.

With a cobalt catalyst, an appreciable amount of branched product forms. If this rearrangement could be influenced so that a branched structure could not form, the yield of linear product would be increased. Collaboration between Union Carbide, Davy McKee, and Johnson Matthey resulted in the adaptation of the so-called Wilkinson catalyst, triphenylphosphine and rhodium chloride, to a homogeneous hydroformylation, in which the ratio of linear-to-branched compounds is 10:1. The mechanism of this linear hydroformylation is shown in Figure 6.15. The reaction takes place at mild temperatures of 100°C and pressures of 10–20 bar. The mild conditions are made possible by the phosphine ligands (represented as L), which increase the activity of the catalyst. It can be seen that the decomposition of the complex **XIX** primarily to the linear (anti-Markownikoff) product results because of the steric requirements of the bulky ligands.

Linear hydroformylation is also an important part of the SHOP (Section 5.3.4) process. However, because of the need in this process to hydroformylate internal olefins with the concomitant shifting of a double bond to the terminal position, a cobalt rather than a rhodium catalyst is used with the ligands that promote linearity.

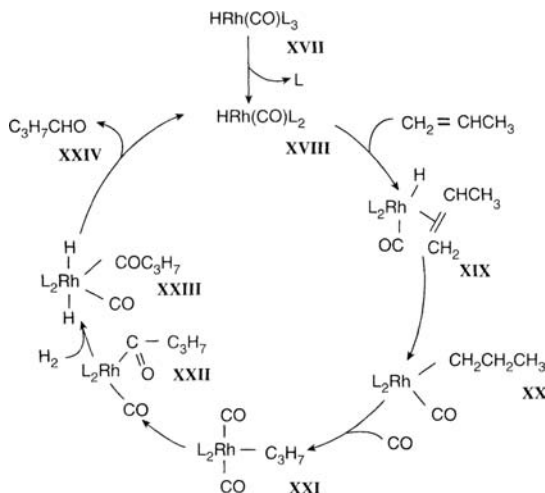
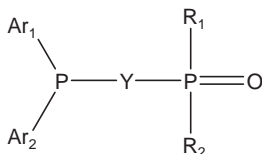


FIGURE 6.15 Linear hydroformylation.

This catalyst is somewhat less effective, giving a ratio of normal-to-iso products of 5.7–6.0:1 and requiring a temperature of 150–190°C at 40 bar.

Newer ligands described by Dow are diphosphine monoxides of the general structure



where the two aryl groups may be the same or different, and R_1 and R_2 may be aromatic or aliphatic. Y is $(\text{CH}_2)_n$. In one example, $\text{Ar}_1 = \text{Ar}_2 = \text{R}_1 = \text{R}_2$ and $\text{Y} = \text{CH}_2$. The ligands give a linear-to-branched ratio as high as 33.8:1.

Even newer ligands developed by Dow and Davy Process Technology (formerly Davy McKee) are bisorganophosphites.

These ligands have a marked stabilizing effect on the catalyst and significantly increase the rate of reaction and linear-to-branched (*n/i*) selectivity. *n/i* Selectivities of over 30:1 are achieved using bisphosphite modified rhodium catalysts. They are so active that over 98% propylene conversion per pass is enjoyed, allowing a “single-pass” process to be used, which simplifies operation and reduces capital cost. In addition, these catalyst systems make possible the hydroformylation under mild conditions of less reactive olefins such as 2-butene, isobutene, and vinyl acetate.

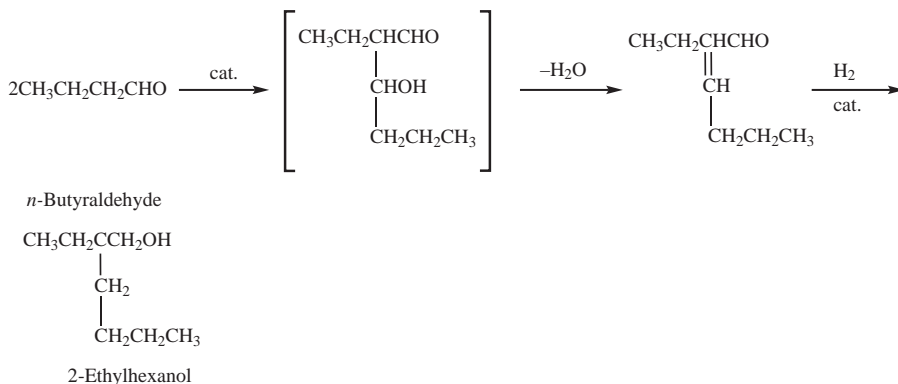
Rhodium is expensive, and efficient catalyst recovery is therefore the key to the success of the process. Two approaches are noteworthy. In the first, described in a Union Carbide patent,²⁵ reaction is carried out in a high boiling solvent comprising butyraldehyde aldol condensate, primarily trimers and tetramers. After reaction, the products can be distilled off, leaving the nonvolatile rhodium complex in the solvent.

The second approach, developed primarily by Rhone Poulenc and Ruhrchemie, involves sulfonated or carboxylated arylphosphine catalysts. After reaction, the organic phase in which the reaction was carried out is treated with alkali. The catalyst is converted to an alkali sulfonate or carboxylate which dissolves in the aqueous layer. Phase separation makes possible catalyst recovery. Another way to cope with the expense of rhodium is to make the catalyst so active that only an insignificant amount is used per pound of product. Today's oxo technology has made important strides in this direction.

6.9.1 Uses for Butyraldehyde, Isobutyraldehyde, and *n*-Butanol

The reason a high linear-to-branched ratio is desired is because the major use of the aldehydes is for hydrogenation to the corresponding alcohols, which are used as solvents either as such or more often in the form of their acetates. *n*-Butanol, because of its linearity, solvates better than the branched isobutanol and is accordingly preferred, particularly for solvents for surface coatings. It is prepared by hydrogenation of *n*-butyraldehyde in the gas phase with a nickel or copper catalyst or in the liquid phase with a nickel catalyst. The gas phase requires mild pressures and a temperature of 115–120°C with a nickel catalyst or a temperature of 160°C with a copper catalyst. With a nickel catalyst in the liquid phase, a temperature of 115°C and a pressure of 80 bar are required. Its acrylate is a comonomer in emulsion paints, its phthalate is a PVC plasticizer, and its acetate is a solvent for lacquers and a fruit flavoring (Fig. 6.16).

n-Butyraldehyde will undergo the aldol condensation, in the presence of either sodium hydroxide or a basic ion exchange resin, to provide an intermediate that loses water spontaneously to give an unsaturated aldehyde in quantitative yield. Hydrogenation gives the important plasticizer alcohol, 2-ethylhexanol:



The end-use pattern of 2-ethylhexanol is shown in Figure 6.16. Di(2-ethylhexyl) phthalate (DOP) is the most important PVC plasticizer (Section 11.1.1 and below). There are also other plasticizer esters, such as di(2-ethylhexyl) adipate, tri(2-ethylhexyl) trimellitate, and di(2-ethylhexyl) terephthalate. The acrylate and

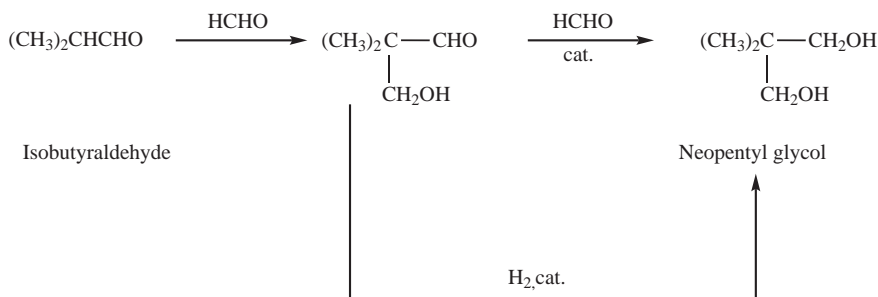


FIGURE 6.16 *n*-Butanol and 2-ethylhexanol demand (2008).

methacrylate esters are used in acrylic emulsion polymers for pressure-sensitive adhesives, textiles, and surface coatings, including high-solids automotive paints. The clean air regulations have increased demand for waterborne acrylic products that replace organic solvent-based products. 2-Ethylhexanol is also used as a low volatility solvent and as an additive for diesel fuel to reduce emissions and to improve the performance of lube oils and mining chemicals.

Because isobutyraldehyde was the surplus coproduct in the classical oxo process, uses were devised for it other than hydrogenation to isobutanol. Conversion to neopentyl glycol (2,2-dimethyl-1,3-propanediol) is the most important. In the most commonly used neopentyl glycol process, isobutyraldehyde reacts with 1 mol of

formaldehyde to yield hydroxypivaldehyde that, after reduction with hydrogen, gives neopentyl glycol. An alternative, less commonly practiced process, is to react isobutyraldehyde with 2 mol of formaldehyde. This approach combines condensation and reduction in one step to yield neopentyl glycol and coproduct formic acid. Neopentyl glycol is used largely in unsaturated polyester synthesis to enhance alkali resistance of the cured product. It is also used to prepare polyesters for powder coating. Its preparation is analogous to that of pentaerythritol (Section 5.11.3).



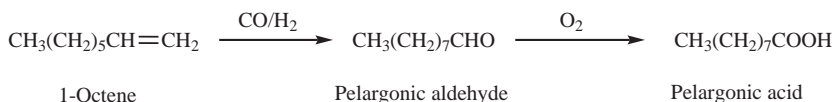
6.9.2 Other Oxo Products

Oxo alcohols are used for solvents, surfactants, and PVC plasticizers. The solvent alcohols, *n*-propanol (Section 5.11.1), butanol, and isobutanol (Section 6.9) have already been discussed. A good example of oxo alcohols for surfactants is those produced by the SHOP process (Section 5.3.4) in which hydroformylation is a major step. Plasticizers are usually esters of phthalic anhydride or less often adipic acid with aliphatic alcohols. Added to poly(vinyl chloride) during compounding, they lend softness and flexibility to the polymer. 2-Ethylhexanol is still the most important plasticizer alcohol in the world, but its use is not growing because of possible toxicity problems with the phthalate plasticizer. Straight-chain alcohols (Sections 4.9 and 6.3) solvate better, so that they have better softening power and compatibility. 2-Ethylhexanol holds its position because of its lower price. Higher molecular weight alcohols are important because their phthalates have better high temperature properties and lower volatility. This helps the “fogged windshield” problem and decreases the rate of embrittlement of plasticized articles because of volatile loss of plasticizer. Meanwhile, the use of PVC in automobile seating is declining. BASF has switched from 2-ethylhexanol to 2-propylheptanol to make the plasticizer called diisononylcyclohexane dicarboxylate for use in sensitive applications where toxicological and exposure issues are of concern. Biobutanol (Section 16.6.5) could be a threat to propylene-based *n*-butanol, if developed commercially as a replacement for MTBE or ethanol as an oxygenate in gasoline.

C₆–C₁₂ olefins for hydroformylation to the plasticizer alcohols as well as C₁₀–C₂₀ olefins for alcohols for nonbiodegradable surfactants come largely from propylene and butene oligomerization (Section 6.3). The most important plasticizer-range alcohols are isodecanol (from propylene trimer) and isononanol (from diisobutene).

Isooctanol (from propylene and butene) and tridecanol (from butene trimer or propylene tetramer) are less widely used. In the UK “Alfanol,” a mixture of C₇–C₉ alcohols, used to be important for plasticizers. ICI made it by application of the oxo process to an olefin mixture from the cracking of a petroleum fraction known as slack wax, but it seems to have disappeared along with its parent company.

A smaller volume use for hydroformylation involves the conversion of 1-octene to pelargonaldehyde. Oxidation of the aldehyde yields pelargonic acid. Reaction with pentaerythritol gives the tetra ester (Section 5.11.3) useful as a component of synthetic lubricants. The oxo catalyst comprises rhodium chloride with triphenylphosphine with or without ferrocene ligand modifiers. The reaction takes place at 5 bar and 100°C. Conversion of 95% of the α -olefin is obtained at a selectivity to the normal aldehyde of 87%. The oxidation is catalyzed by cobalt pelargonate at about 8 bar and 100°C. At 75% conversion of the aldehyde 96% selectivity to the acid is obtained.



6.10 MAJOR CHEMICALS FROM PROPYLENE – A PERSPECTIVE

Sections 6.1–6.9 have described the major chemicals (U.S. production > 500,000 metric tons) from propylene and their derivatives. These major chemicals and their production volumes in 1993, 2001, and 2009, their growth rates, and the amount of propylene used in their production are indicated in Table 6.4. The figures come from a variety of sources and are not necessarily comparable. Note also that 2009 was a year of depression, and the growth rate of the chemical industry is not as bad as the figures suggest.

Meanwhile, polypropylene is still the largest use and has consolidated its position. Cumene, which used to be the second largest use, has been overtaken by propylene oxide. Propylene oxide reacts to give hydroxyl-terminated oligomers, which are the major coreactants with isocyanates for polyurethane polymers. Acrylic acid appears in numerous esters and surface coatings and feeds a growth market for superabsorbent polymers. Acrylonitrile had a bad year in the United States compounded by the movement of the textile industry to Asia-Pacific. It is also used for elastomers and for acrylonitrile–butadiene–styrene resins familiar to everyone who uses computers or telephones.

Cumene is the progenitor of phenol (Section 9.1) and acetone. Acetone is used as a solvent, but its important chemical use is as a starting material for methyl methacrylate, which in turn is polymerized to poly(methyl methacrylate) and related copolymers. Competitive routes based on C₂ and C₄ olefins for methyl methacrylate exist and the figures here represent total, global methyl methacrylate production. Acetone and phenol are the starting materials for bisphenol A, which in turn is

TABLE 6.4 Summary – United States, Western Europe, and Asia-Pacific

Polymer or Chemical	United States (million metric tons) 1993	United States (million metric tons) 2001	United States (million metric tons) 2009	Western Europe (metric tons) 2009	Asia-Pacific (metric tons) 2009	Propylene Used, United States ^a	Average Annual Increase(%), United States 2001–2009
Propylene	10.16	14.38	11.90	15.10	32.40		–2.34
Polypropylene	3.91	7.14	7.54	8.69	22.40	7.54	0.68
Cumene	2.04	3.72	2.71	1.53	2.34	0.36	–3.90
Phenol ^b	1.69	2.19	1.80	2.35	3.60		–2.40
Propylene oxide	1.50	1.92	3.70	2.23		1.43	8.55
Acrylonitrile	1.14	1.52	1.11	0.63	3.25	1.07	–3.87
Acetone	1.12	1.46		1.53			
Oxo alcohols including	0.98 0.60		0.88	0.40		0.71	0.75
<i>n</i> -Butanol							
2-Ethylhexanol	0.31	0.40	0.28	0.47		0.24	–4.55
Acrylate esters	0.60	0.71					
Bisphenol A	0.58	0.89	0.95	1.02			0.71
Isopropanol	0.56	0.66					
Acrylic acid	0.54	0.88	1.17	0.83		0.71	3.69
Methyl methacrylate	0.49	0.68	3.6(global)				
Propylene glycol	0.40	0.52		0.59			

^a This is the propylene required to give the 2009 production. Yields assumed 100% if no other information available.

^b Phenol is really a benzene derivative. Although coproduced with acetone, it contains none of the propylene moiety.

Source: Chemical Engineering News, Guide to the Business of Chemistry, and miscellaneous sources, not necessarily comparable.

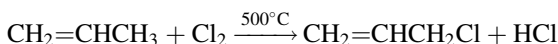
combined with another propylene-based chemical, epichlorohydrin, to make epoxy resins. More important is its reaction with phosgene, CoCCl_2 , to yield polycarbonate resins (Section 9.1.2.2).

The demand these chemicals make on propylene supplies is shown in the final column of Table 6.4. As might be expected, polypropylene is the biggest consumer of propylene; propylene oxide is next and then acrylonitrile. There are a substantial number of minor uses such as epichlorohydrin, ethylene-propylene elastomers, acrolein, allyl chloride, and isopropyl acetate. Some of the smaller volume chemicals from propylene are described in Section 6.11.

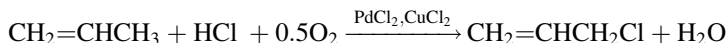
6.11 LESSER VOLUME CHEMICALS FROM PROPYLENE

6.11.1 Allyl Chloride and Epichlorohydrin

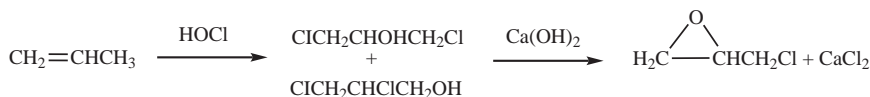
Allyl chloride is formed by the selective chlorination of the methyl group of propylene at 500°C . The high temperature prevents addition to the double bond. Propylene and chlorine conversions are about 24% and 100%, respectively, at an allyl chloride selectivity of 86 mol%. By-products include dichloropropenes and minor amounts of isopropyl chloride and other chlorinated compounds.



An as yet uncommercialized oxychlorination route to allyl chloride catalyzed by palladium and cupric chlorides (Section 5.4) has been devised. It proceeds at a much lower temperature of 240°C :



The epoxidation of allyl chloride to epichlorohydrin proceeds like the traditional route to propylene oxide (Section 6.8). Treatment of allyl chloride with hypochlorous acid gives 1,3-dichloro-2-hydroxypropane $\text{ClCH}_2\text{CHOHCH}_2\text{Cl}$ and 1,2-dichloro-3-hydroxypropane $\text{ClCH}_2\text{CHClCH}_2\text{OH}$ in a ratio of 9:1. These react below 60°C with a 10–15 wt% aqueous slurry of calcium hydroxide to give almost 100% conversion to epichlorohydrin.



In the overall process for epichlorohydrin from propylene, 75% of the chlorine is wasted; that is, it does not appear in the final product.

Dow has patented a route to epichlorohydrin based on addition of chlorine to acrolein, followed by hydrogenation of the aldehyde group to the corresponding alcohol and finally undergoing dehydrohalogenation to give epichlorohydrin.²⁶

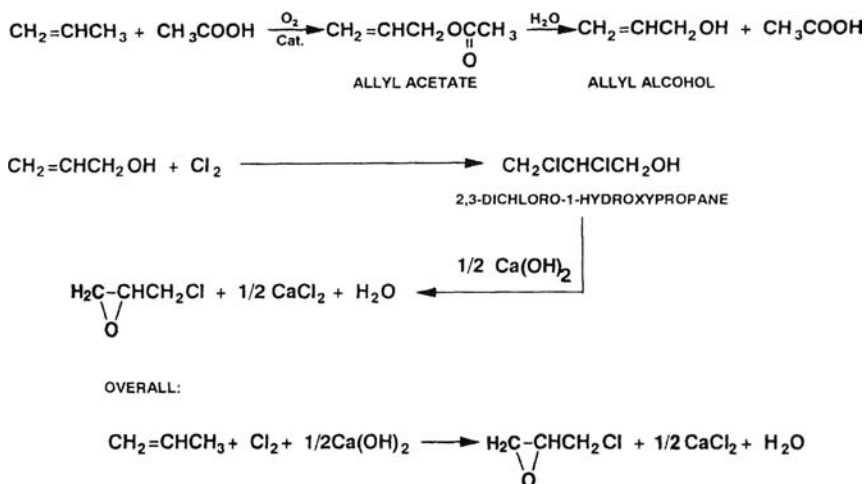
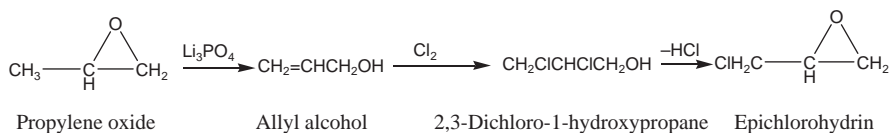
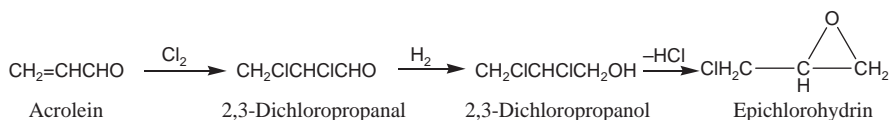


FIGURE 6.17 Showa Denko epichlorohydrin process.

Because epichlorohydrin is made in far smaller quantities than ethylene and propylene oxides, the search for a replacement for the chlorohydrin process was less strongly motivated. Nonetheless, in the mid-1980s a process was instituted by Showa Denko in Japan. This process wastes only 50% of the chlorine. Propylene is oxidized to allyl acetate by oxygen in acetic acid with a palladium catalyst as shown in Figure 6.17. Hydrolysis yields allyl alcohol and acetic acid for recycle. There are other routes to allyl alcohol. In addition to direct oxidation, allyl chloride can be hydrolyzed to allyl alcohol by 5–10% caustic soda at 150°C and 13–14 bar. Acrolein, also obtained by the oxidation of propylene (Fig. 6.4c), can be converted to allyl alcohol by the Meerwein Ponderoff reduction (isopropanol plus aluminum isopropoxide) as shown in Figure 6.18. There is also a curious isomerization of propylene oxide over lithium phosphate that gives allyl alcohol. The allyl alcohol is treated with chlorine and the resulting 2,3-dichloro-1-hydroxypropane is dehydrohalogenated to epichlorohydrin.



Dow was granted a patent that uses acrolein as the starting material for making epichlorohydrin. Addition of chlorine to acrolein gives 2,3-dichloropropanal. The dichloropropanal is hydrogenated to 2,3-dichloropropanol, which in turn undergoes dehydrohalogenation with calcium hydroxide finally to give epichlorohydrin.



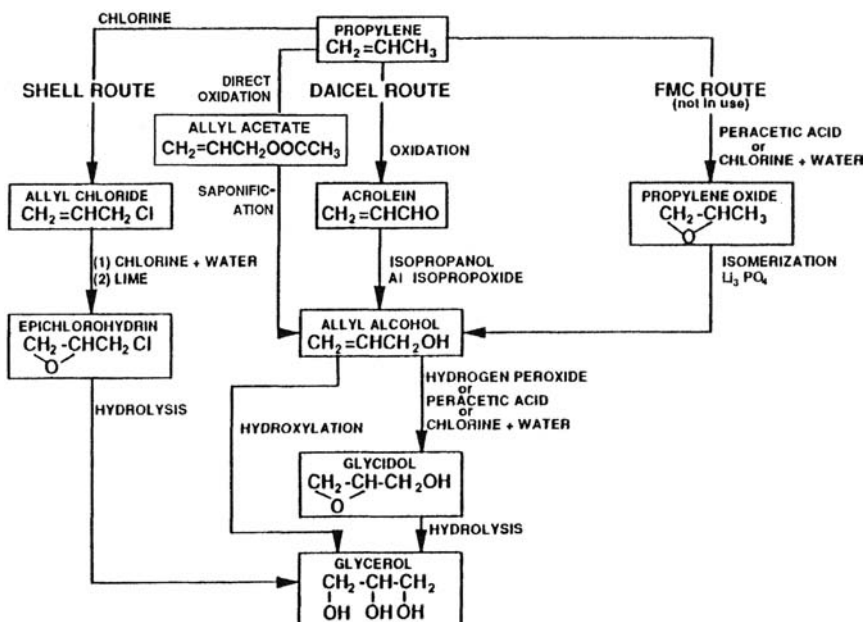
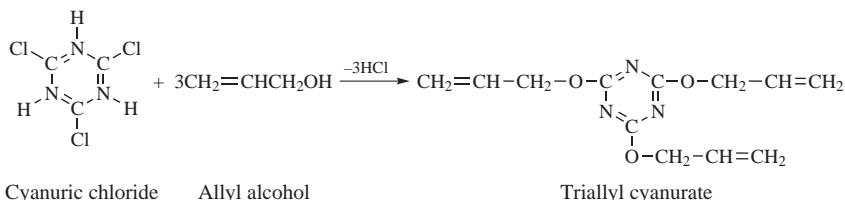


FIGURE 6.18 Synthetic routes to epichlorohydrin, allyl alcohol, and glycerol.

A new approach for making epichlorohydrin starts with glycerol. Just as the glut of biodiesel-based glycerol has spurred development of new routes to propylene glycol (Section 6.8.2), the availability of low priced crude biodiesel glycerol has prompted the development of new technology for converting glycerol to epichlorohydrin. Solvay is reportedly building a 100,000 metric ton/year plant for carrying out this conversion in China, due on stream in 2013.²⁷ The idea of converting glycerol to epichlorohydrin is curious in that “synthetic” glycerol had historically been made from epichlorohydrin (Fig. 6.18).

Epichlorohydrin’s major use is its reaction with bisphenol A (Section 9.1.2) to yield epoxy resins. It also played a role in glycerol synthesis (Section 6.11.2). The major use of allyl alcohol was similarly in glycerol preparation but, with the glycerol surplus, these last two epichlorohydrin uses have all but disappeared. Allyl alcohol reacts with phthalic anhydride to yield diallyl phthalate, a monomer for a thermoset polymer with good electrical properties, and with cyanuric chloride, to give triallyl cyanurate a polyester for thermoset resins with high heat resistance.



Allyl chloride is converted by ammonia to mono-, di-, and triallylamines.

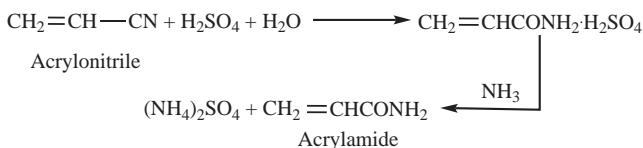
6.11.2 Glycerol

Natural fats and oils are triglycerides (Chapter 15) and give glycerol²⁸ on hydrolysis or methanolysis. Soap, oleochemical, and biodiesel production all produce glycerol as a by-product. These applications now supply virtually all of the world's glycerol. Before the advent of biodiesel, about a quarter of glycerol came from chemical synthesis. The routes are summarized in Figure 6.18. The most important process (Fig. 6.18, Shell route) involves simply the hydrolysis of epichlorohydrin with 10% aqueous caustic soda at 150°C. Complete conversion is obtained. The reaction goes stepwise, the chlorine atom hydrolyzing first.

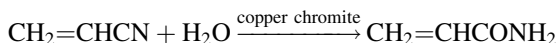
A route via acrolein (Fig. 6.18, Daicel route) involves a Meerwein–Ponndorf reduction of acrolein to allyl alcohol (see above), which is epoxidized with hydrogen peroxide, hypochlorous acid, or peracetic acid, to glycidol, whose hydrolysis yields glycerol. Alternatively, the allyl alcohol may be hydroxylated to glycerol directly. In the early 1990s, Daicel modified its process by oxidizing propylene directly to allyl acetate (Section 6.11.1), which on saponification yields allyl alcohol, as in the Showa Denko process (Fig. 6.17). This is an efficient route, but one that requires high capital investment. In the FMC route, shown in Figure 6.18 but no longer in use, propylene oxide is isomerized with a lithium phosphate catalyst to allyl alcohol. This can be converted to glycerol by the process already described. It is of interest that ARCO has adapted this route to allyl alcohol for a synthesis of 1,4-butanediol (Section 12.3.1). Glycerol's uses are reviewed in Section 15.11. The pattern of glycerol manufacture varies around the world depending on indigenous production of fats and oils. Synthetic glycerol was manufactured in the United States only by Dow. Its greater purity earned for it applications in cosmetics and personal care products, but currently Rohm and Haas and Novosep are said to be studying the purification of biodiesel by-product glycerol.

6.11.3 Acrylamide

Hydrolysis of acrylonitrile with sulfuric acid gives acrylamide:

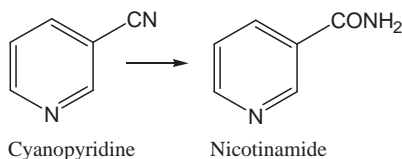


As in the synthesis of caprolactam (Section 9.2.2) an undesirable low value by-product, ammonium sulfate, is generated, whose separation from the acrylamide is complex. This process has largely been replaced by an elegant catalytic hydrolysis using metallic copper. The reaction takes place at 100°C and gives almost 100% selectivity at 60–80% conversion.



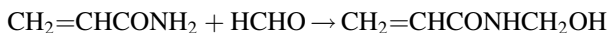
In the early 2000s, CDTECH, in collaboration with SASTECH (the technology arm of Sasol Industries), developed a process for acrylamide, similar to the above but using catalytic distillation to reduce the number of process steps, with savings in energy and equipment.²⁹

Nitto in Japan has developed a microbiological conversion of acrylonitrile to acrylamide.³⁰ At the time of writing, it provides the only example of the application of modern microbiology to the production of a reasonably large volume chemical other than fermentation-produced ethanol and high fructose corn syrup (Section 16.3). This conversion is brought about by an immobilized bacterial cell (e.g., species of nocardia, microbacterium, and corynebacterium) that contains the hydrolyzing enzyme. A temperature of 10°C and a pH of 7.5 lead to a 15% aqueous solution of acrylamide in quantitative yield. At least six plants were using this process in the early 2000s. The process has since been extended to the synthesis of nicotinamide (niacinamide, part of the vitamin B complex) from cyanopyridine:



Most acrylamide is polymerized to a water-soluble polymer. Anionic character may be conferred by partial hydrolysis of amide linkages to carboxyl groups. Anionic functionality can also be achieved by copolymerization of acrylamide with monomers such as sodium acrylate. Conversely, monomers such as dimethylaminoethyl acrylate impart cationic character.

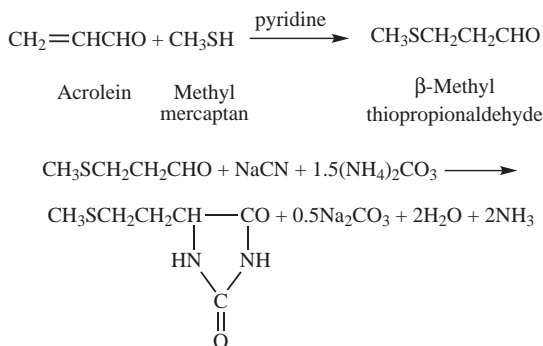
A potentially important use for the polymers is in enhanced oil recovery where they increase the viscosity of the water used for the flooding that pushes oil through the rock formation so that it can be pumped. Their major use is for flocculants in industrial and municipal waste water treatment. They are included in formulations for paper and textile sizing, drilling muds for oil well drilling, ore processing, and in the coagulation of slimes. They are of value in gel electrophoresis. With other acrylic monomers, acrylamide provides copolymers useful in the formulation of water-based protective coatings. If the amide group is converted to a methylol group with formaldehyde, a compound results that can crosslink with melamine resins (Section 12.5.1.3).



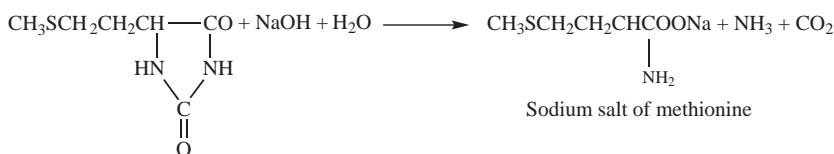
Acrylamide has been found in minute quantities in carbohydrate foods that have been fried or roasted or heated generally, such as potato chips, French fries, and bread. In large doses, it causes cancer in rats, but the dose that gives cancer to 10% of rats is 900 times what a human might consume on a weight-for-weight basis, and there is no evidence that it causes cancer in humans. Nonetheless, the European Chemicals Agency placed it on its list of substances of “very high concern” in March 2010.

6.11.4 Acrolein

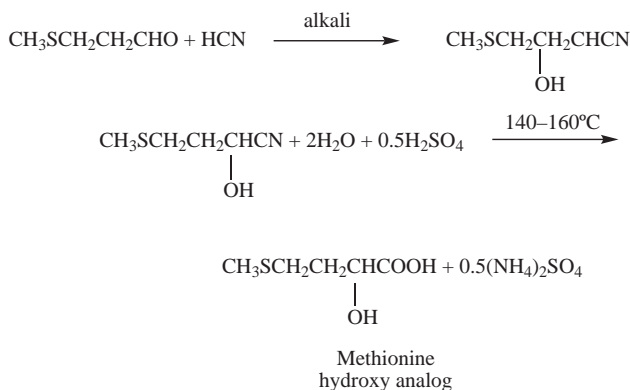
The preparation of acrolein as an intermediate in acrylic acid production was described in Section 6.4. Its role in glycerol synthesis was described in Section 6.11.2. The most important use for acrolein, however, is for the manufacture of DL-methionine, an essential amino acid added to poultry feeds. Methionine is the amino acid produced in third largest volume after L-glutamic acid, whose monosodium salt is a flavor enhancer in foods and L-lysine, also used in feeds. In the methionine synthesis, acrolein reacts almost quantitatively with methyl mercaptan in the presence of pyridine to yield β -methylthiopropionaldehyde. The aldehyde is converted to a hydantoin with sodium cyanide and ammonium carbonate.



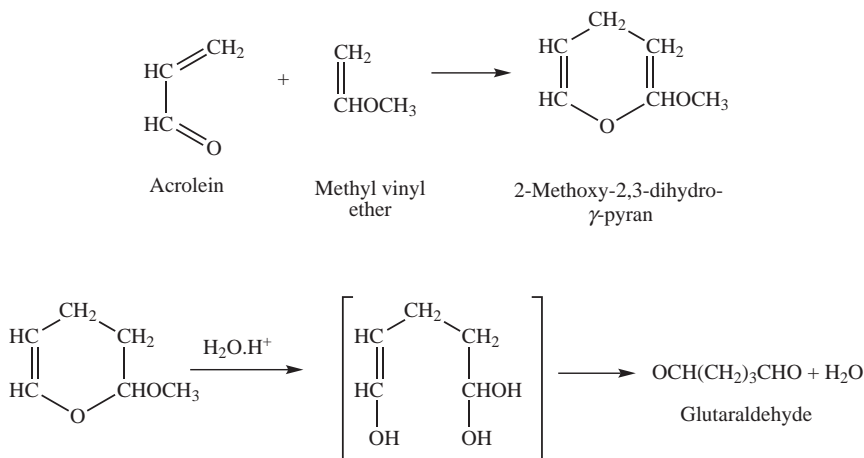
Aqueous hydrolysis of the hydantoin with sodium hydroxide and sodium carbonate at 6 bar provides the sodium salt of methionine with the release of ammonia.



The sodium salt is then acidified and the methionine precipitates at its isoelectric pH of 5.7. The product of commerce is DL-methionine, the D-isomer being converted in the organism to the useful L-structure. Also effective in feeds is the DL-methionine hydroxy analog developed by Monsanto. It is prepared by a simpler process, since an amino group does not need to be inserted into the molecule. This process too goes via β -methylthiopropionaldehyde, whose quantitative reaction with hydrocyanic acid at 40°C gives a cyanohydrin that can be hydrolyzed with sulfuric acid at 140–160°C and 3–4 bar to DL-methionine hydroxy analog. The product is sold in aqueous solution.



Glutaraldehyde is manufactured in small quantities from acrolein, which undergoes a Diels–Alder reaction with methyl vinyl ether (Section 5.11.11) to yield 2-methoxy-2,3-dihydro- γ -pyran, whose hydrolysis in the presence of acid yields glutaraldehyde.

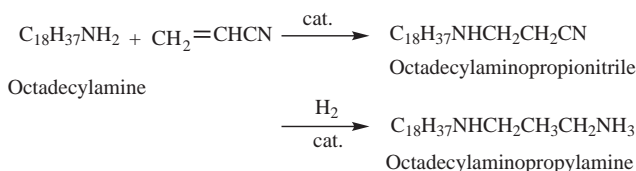


Glutaraldehyde is one of the two dialdehydes available commercially, the other being glyoxal (Section 5.11.6.7). They are useful for crosslinking hydroxyl-containing materials like leather or cellulose, and for textile and paper treatment. They are also used in the immobilization of enzymes (Section 18.8).

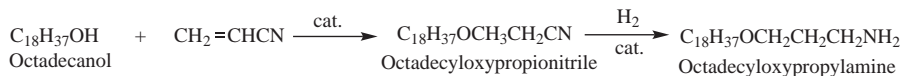
A “new” use for acrolein is as an intermediate for making 1,3-propanediol. Addition of water to acrolein gives 3-hydroxypropionaldehyde. This is the same material that Shell makes by hydroformylation of ethylene oxide (Section 5.11.6.6). Hydrogenation of 3-hydroxypropionaldehyde yields the promising new polyester monomer 1,3-propanediol (Section 5.11.6.6).

6.11.5 Acrylonitrile Derivatives

Acrylonitrile production was described in Section 6.5 and its most important uses have been discussed in Sections 6.5.1. It also participates in a reaction called cyanoethylation. A compound with a reactive hydrogen atom undergoes a base-catalyzed Michael addition to its double bond. A quaternary ammonium base such as trimethylbenzylammonium hydroxide is an excellent catalyst. Typical reactions are those with fatty amines and fatty alcohols. Reaction with octadecylamine yields octadecylaminopropionitrile. On hydrogenation this yields octadecylaminopropylamine, a corrosion inhibitor valuable in the oil drilling industry.



The reaction with octadecanol provides cyanopropyl octadecyl ether whose nitrile group can also be hydrogenated to an amine. This compound is a flotation agent for the removal of silica from iron ore.



The graft polymerization of acrylonitrile onto starch provides a polymer capable of absorbing many times its own weight of water (Section 6.4.1), once the nitrile groups are partially hydrolyzed to amides and carboxyls.

ENDNOTES

1. J. Mark Houdek and J. Andersen, "On-Purpose" Propylene – Technology Developments, UOP LLC, 25 East Algonquin Road, Des Plaines, Illinois, USA. See also Nexant ChemSystems PERP report 97/98S3, *Routes to Propylene* (July 2000).
2. Catalysts and operating conditions for deep catalytic cracking process is described in European Patent 0 305 720 B1 (13 April 1994) assigned to RIPP and Sinopec.
3. A. H. Tullo, *Chem. Eng. News*, 18 October 2010, pp. 10–16.
4. Selective vapor phase oxidation of propylene to acrolein in a recirculating solids reactors is the subject of a patent assigned jointly to DuPont and Elf Atochem. World Patent 99/03809 (28 January 1999). This approach is similar to that developed by DuPont for oxidizing *n*-butane to maleic anhydride. The advantage to this is that by avoiding oxygen in the gas phase, the riser reactor enables greater selectivity to acrolein.
5. For example, U.S. Patent 6,043,184 (28 March 2000) to Sunoco and Rohm and Haas.
6. Johnathan E. Holladay, Michael A. Lilga, and Todd A. Werpy, iic.pnl.gov/abstracts/nacs/o_109.pdf.

7. World Patent 2009/045637 (9 April 2009) to Genomatica, Inc.
8. http://en.wikipedia.org/wiki/Grubbs'_catalyst.
9. *Chem. Eng. News*, 22 December 2008.
10. U.S. Patent Application 2008/0183013 A1 (31 July, 2008) to Arkema.
11. *Chem. Ind.*, 2 September 2002, p. 12, and www.celanese.com/celanese_in_depth_2001_chemical_intermediates.pdf.
12. Patents with promising results are U.S. Patent 5,895,635 (20 April 1999) to Standard Oil Company and Japanese Patent 10-028862 (3 February 1998) to Mitsubishi Chemical Corporation.
13. The ICI route to hexamethylene diamine via acrylonitrile coupling has been described in *Chemical Week*, 7 March 1990, p. 9.
14. For an overview see Nexant ChemSystems PERP report 01/02-2, *Phenol/Acetone/Cumene* (September 2002). Also H. Wittcoff, *J. Chem. Ed.* **56**, 810, 1979.
15. The Sumitomo technology is described in WO 03027087A1 (3 April 2003) to Sumitomo Chemical Company Limited.
16. Nexant ChemSystems PERP report 99/00-2, *Methyl Methacrylate* (September 2001) assesses the myriad approaches. See also M. Morgan, *Eur. Chem. News*, 11–17 February 2002, pp. 20–23.
17. U.S. Patent 6,042,472 (21 March 2000) to Asahi Kasei Kogyo Kabushiki Kaisha.
18. ICI/INEOS methyl propionate/condensation reaction is described in WO 99/52628 (21 October 1999) to Imperial Chemical Industries, PLC.
19. Nexant ChemSystems PERP report 08/09-7, *Methyl Methacrylate*, March 2010. <http://www.icis.com/Articles/2010/10/25/9403882/aveneer-key-to-evoniks-future.html>.
20. New routes to propylene oxide are summarized by S. Robinson, *European Chemical News*, 5–11 March 2001, pp. 19–20.
21. The use of hydrogen peroxide as an oxidant to make propylene oxide is described in WO 03011845A1 (1 February 2003) to BASF.
22. http://www.solvay.com/EN/NewsPress/Documents/2008/20080930_Investorsday_E.Mignonat.pdf.
23. http://www.solvay.com/EN/NewsPress/Documents/2008/20080930_Investorsday_E.Mignonat.pdf.
24. <http://www.inchem.org/documents/sids/sids/pges.pdf>.
25. *Chem. Eng. News*, 10 October 1988, p. 270.
26. U.S. Patent 6,008,419; (28 December 1999) to Dow Chemical Company.
27. *Chem Week* 7/14 February 2011, p. 21.
28. Industrial glycerol is known as glycerin or glycerine. We are reluctant to make this distinction and prefer glycerol, because the “ol” suffix hints at the presence of hydroxyl groups.
29. K. Rock, J. Almering, and S. Swart, *Conversion of Acrylonitrile to Acrylamide via Catalytic Distillation*, European Petrochemical Technology Conference, June 2001.
30. U.S. Patent 5,698,629 (16 December 1997) to Nitto Chemical.

CHAPTER 7

Chemicals from the C₄ Stream

We have described the huge volume of chemicals based on ethylene and the somewhat smaller volume based on propylene. Quantitatively the C₄ stream provides far less chemicals than ethylene or propylene. Only three C₄-based chemicals – butadiene, isobutene, and methyl *t*-butyl ether (MTBE) – are among the 50 chemicals produced in highest volume around the world, and MTBE is declining rapidly and will soon not make the list. C₄ stream usage is not in the same league as 2009 consumption of ethylene (114 million metric tons) and propylene (70 million metric tons). About 10 million metric tons of butadiene were consumed globally in 2009. Relatively small amounts of isobutene are required for chemical uses (methyl methacrylate and butyl rubber) but there is still a demand for it as a feedstock for MTBE in unleaded gasoline. In the late 1980s and 1990s, MTBE was the fastest growing chemical ever. Global demand for MTBE in 2009 was approximately 13 million tons per year (about 1.4% of global gasoline volume), after having peaked at over 23 million tons in 2002, before its use in California was banned from January 2004. One ton of MTBE requires 0.64 ton of isobutene; thus current demand for isobutene for MTBE production is about 8.3 million metric tons.

Because of the environmental issues associated with MTBE, its use in the United States has all but ceased. There is potential litigation over product liability, and legislative changes affecting reformulated gasoline requirements. Meanwhile, in 2009, several U.S. companies were still producing MTBE, either to make high purity isobutene (via back cracking MTBE made from Raffinate I – see below) or for use as a gasoline blendstock in export markets. Mexico and Venezuela are the key destinations.

Butadiene goes mainly into synthetic rubbers. There is a range of these of both chemical and historical importance. It was the C₄ stream that provided the synthetic rubber vital to both sides in World War II. Although the C₄ stream tonnage is relatively low, its chemistry is interesting and different, so we shall deal with it in comparable detail.

Steam cracking of natural gas gives far less C₄ fraction than does naphtha cracking (Section 4.3). *n*-Butane, traditionally, has seldom been cracked in the United States, because there is little of it in natural gas. What there is was used largely for fuel for heating and cooking. This application in the United States increased in the mid-1980s because butane supplies are being augmented by its removal from gasoline. Particularly in the summer, it volatilizes from gasoline and damages the ozone layer. A more important recent source of *n*-butane is LPG (Section 4.1), which is finding greater use as cracking feedstock. A C₄ unsaturated fraction is also obtained from catalytic cracking. However, this fraction is dilute, and isolation of chemicals from it is more expensive. Most of it is used for alkylation (Section 4.10).

Because the United States has traditionally cracked natural gas fractions, there has always been a shortage of butadiene. The shortfall was accommodated by imports from Asia and Western Europe where naphtha cracking yields an excess of the C₄ fraction. Asian supplies have recently diminished because of demands in East Asia and India. Indeed, East Asia became an importer of butadiene in the early 2000s. In the days of a European butadiene surplus, five companies were motivated to convert butadiene to *n*-butenes, useful for alkylation. Now, however, butadiene is in very short supply for two main reasons. First, a tremendous amount of new ethylene capacity has recently come on stream in the Middle East. These huge crackers crack light feedstocks such as ethane and propane. Not only do they not make much butadiene, but they have forced a lot of older, smaller, and higher cost plants primarily fed by naphtha to shut down in other regions of the world. Second, the U.S. crackers that are flexible and can run on either gas or liquid feeds chose to crack gaseous feeds when gas prices plummeted in 2009 and 2010 because of the new gas supplies coming into the market from shale gas. This has also reduced butadiene supplies. Butadiene prices have soared and this is stimulating development of “on-purpose” butadiene process technologies. Butene and butane dehydrogenation technologies are being revisited.

The main components of the C₄ stream are *n*-butane, 1-butene, 2-butene, isobutene, and 1,3-butadiene. Table 7.1 shows a typical composition of the C₄ fraction from steam cracking. These can to some extent be interconverted (Fig. 7.1). *n*-Butane readily isomerizes to isobutane, which can be dehydrogenated to isobutene, a process commercialized in the early 1990s to obtain isobutene for MTBE. Both *n*-butane and the butenes can be dehydrogenated to 1,3-butadiene. Dehydrogenation of butenes is practiced in the United States when it is favored by a high butadiene price. It is harder to dehydrogenate *n*-butane, and this is not currently done, although it was in the past.

Like propylene, the butenes have both fuel and chemical uses. When reacted with isobutane (Section 4.10) they provide alkylate for gasoline. When dimerized they become a component of high octane polymer gasoline. Hydrogenation is not strictly necessary, although the double-bonded compounds tend to form tars. The dimers can be hydroformylated (Section 6.9.1) to provide nonanol for plasticizers (Section 9.1.1). Newer methods of dimerization (Section 7.1.6.2) yield more nearly linear products, which give more effective plasticizers. Alkylate has no chemical uses.

The separation of the C₄ olefins is complex and is outlined in Figure 7.2. The first step is removal of 1,3-butadiene by extractive distillation with an aprotic solvent, usually acetonitrile, *N*-methylpyrrolidone, or dimethylformamide. Each of these

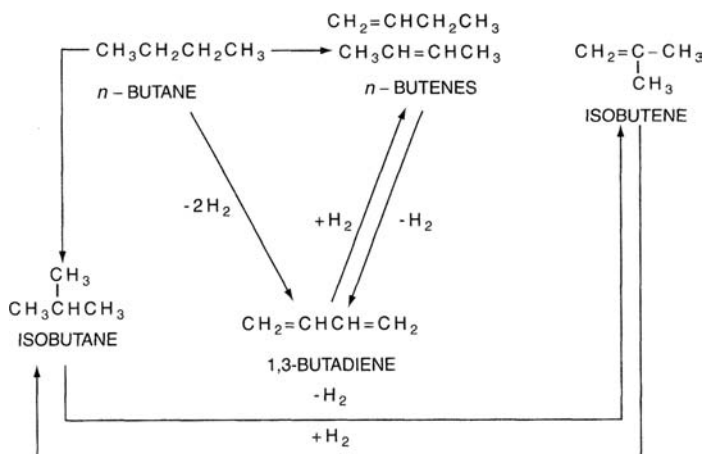
TABLE 7.1 Typical Composition of the C₄ Fraction from Steam Cracking of Naphtha

Component	Cracking Severity	
	Medium (weight percent)	High (weight percent)
C ₃ s	0.3	0.3
<i>n</i> -Butane	5.2	2.8
<i>i</i> -Butane	1.3	0.6
1-Butene	16.0	13.7
<i>cis</i> -2-Butene	5.3	4.8
<i>trans</i> -2-Butene	6.6	5.8
Isobutene (methylpropene)	27.4	22.2
1,3-Butadiene	37.0	47.5
Methylacetylene	100 ppm	100 ppm
Vinylacetylene	0.3	1.6
Ethylacetylene	0.1	0.2
C ₅ s	0.5	0.5

solvents is effective in depressing the volatility of components other than butadiene. However, a small amount of butadiene is left in the raffinate, which must be removed by after-treatment (selective hydrogenation) if pure 1-butene is desired later in the process.

The butadiene-free raffinate that results is called and traded as Raffinate I. It contains the two *n*-butenes and isobutene. The isobutene is reactive and may be separated by hydration to *tert*-butanol in the presence of sulfuric acid or, in more modern plants, by use of a fixed bed catalyst. *tert*-Butanol may be used as such or it may be dehydrated to pure isobutene.

In an alternative process, Raffinate I reacts with methanol to give MTBE. This usually is used as such but, like *tert*-butanol, it may be cracked to give pure isobutene.

**FIGURE 7.1** Major components of the C₄ stream.

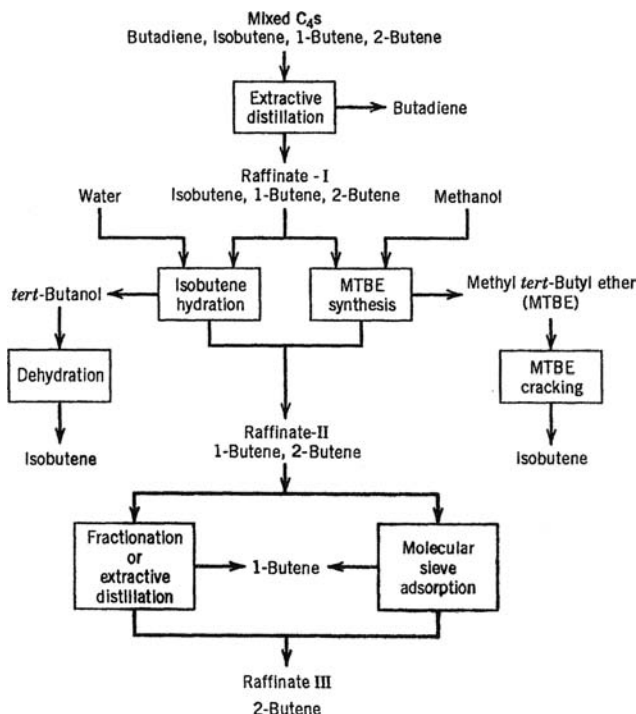


FIGURE 7.2 Separation of the C₄ olefins stream.

The etherification process to MTBE is highly selective, on a par with the carboxylation of methanol to acetic acid (Section 12.5.2.2). It goes to about 97% conversion and, if all the isobutene must be removed, a second step is necessary in which the Raffinate I is reacted with a large excess of methanol.

Other processes for removing the isobutene involve an acid-catalyzed dimerization at 100°C to form isomers of 2,2,4-trimethylpentene, useful for the gasoline pool. Another possibility is the polymerization of the isobutene to polyisobutene. The polymerization is catalyzed by aluminum chloride and the polymer is useful in adhesive and sealant formulations and petroleum product additives (Section 5.2.3).

The mixture of 1- and 2-butenes that remains is called and traded as Raffinate II. It may be hydrated to *sec*-butanol (Section 7.3) or oxidized to maleic anhydride (Section 7.4.2), although the latter is not done in the United States. In the process, 1-butene isomerizes to the more stable 2-butene.

The two butenes in Raffinate II may also be separated to yield pure 1-butene for linear low density polyethylene production (Section 5.1.4). There are three procedures for separating the isomers. Fractionation requires a high multi plate low temperature column because the boiling points are −6.47°C (1-butene) and 3.73°C (*cis*-2-butene). Use of extractive distillation and molecular sieve absorption (UOP's Sorbutene process) is also possible. The advantage of the UOP process is that pure 1-butene results even if appreciable isobutene remains in the Raffinate II. The other

two processes are useful only if the butadiene and isobutene contents of Raffinate II are low. The *cis* and *trans* 2-butene stream that results is called Raffinate III. The pure isomers do not have many uses and the material is not ordinarily purified but is sent to the alkylation unit.

7.1 CHEMICALS AND POLYMERS FROM BUTADIENE¹

The United States and Western Europe traditionally have used the C₄ stream differently. In Europe there is an excess of gasoline relative to diesel fuel and fuel oil. Hence there is only a small market for alkylate gasoline. Furthermore, naphtha is the major feedstock for steam cracking, and Western Europe's requirements for 1,3-butadiene can be satisfied by extraction from the copious C₄ stream that naphtha cracking produces. Hence, there is little demand for butenes and little difference in value between them and butanes. In the United States, on the other hand, alkylate gasoline is in ever greater demand for unleaded gasoline, and butenes are also required for dehydrogenation to butadiene, which is not provided in sufficient quantities by steam cracking of natural gas liquids. Therefore, the butenes have greater value.

Figure 7.3 shows butadiene's end-use pattern in the United States, Western Europe, and Asia-Pacific. About 54% goes into synthetic rubbers, down from 70% a decade ago. Table 7.2 lists the major elastomers and their compositions. Figure 7.3 also illustrates dramatically the growth of the Asia-Pacific market for elastomers. Consumption is over twice that of the United States and Western Europe put together.

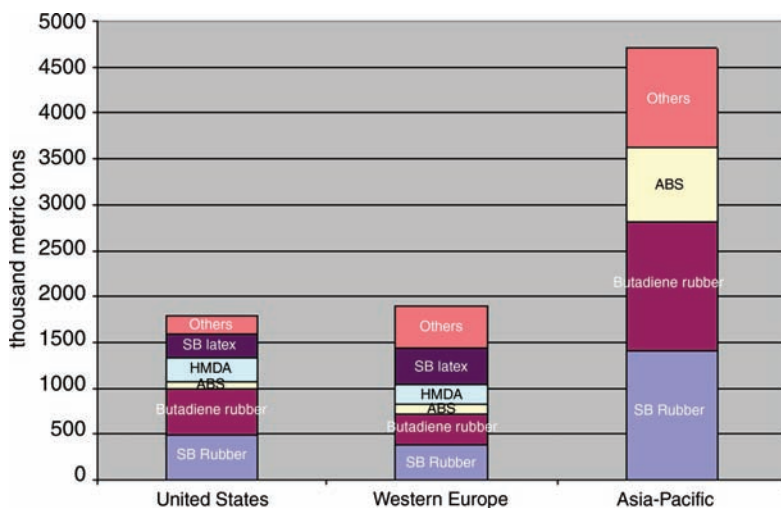



FIGURE 7.3 Butadiene demand pattern (2009). "Others" includes polychloroprene, nitrile, and ethylene-propylene rubbers. In the Asia-Pacific statistics, it includes SB latex and HMDA. Note that the figures refer to butadiene consumed, not to the volume of copolymers produced. (Source: Nexant Inc.)

TABLE 7.2 Major Elastomers

Elastomer	Monomers and/or Structure	Polymerized by	Comments
Natural rubber	<i>cis</i> -1,4-Polyisoprene $\left[\begin{array}{c} \text{H}_2\text{C} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H}_3\text{C} \quad \text{H} \end{array} \text{CH}_2 \right]_n$	Enzymes	Obtained from <i>Hevea brasiliensis</i>
Styrene-butadiene rubber (SBR)	~1 mol styrene to 6 mol butadiene $\text{CH}=\text{CH}_2$  $+ \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	Emulsion polymerization, free radical initiator often at low temperature (cold rubber)	~20% Butadiene units are in 1,2-configuration, ~60% are <i>trans</i> -1,4 and 20% <i>cis</i> -1,4
<i>cis</i> -1,4-Polybutadiene rubber	$\left[\begin{array}{c} \text{CH}_2 \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array} \text{CH}_2 \right]_n$	Metal complex	High resiliency
Butyl rubber (Section 7.2.2)	Isobutene + 1–3% isoprene $\text{CH}_2=\text{C}(\text{CH}_3)_2$ $+ \text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$	Cationic initiator	High gas impermeability
Synthetic <i>cis</i> -1,4-polyisoprene	Isoprene $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$	Metal complex	Properties similar to natural rubber

Polychloroprene rubber	Chloroprene $\left[\text{CH}_2 - \underset{\text{Cl}}{\text{CH}} = \text{C} - \text{CH}_2 \right]_n$	Free radical initiator	Excellent ozone resistance
Nitrile rubber	<i>trans</i> -1,4-Polychloroprene Butadiene + 20–40% acrylonitrile $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ + $\text{CH}_2 = \text{CHCN}$	Free radical initiator	Similar to SBR but better oil resistance
Ethylene–propylene (EP) rubber and ethylene–propylene diene monomer (EPDM) rubber	In EP, C ₂ H ₄ and C ₃ H ₆ . In EPDM, ethylidene norbornene, <i>trans</i> -1,4-hexadiene (Section 7.1.66) or dicyclopentadiene (Section 8.1) is added.	Metal complex	EP vulcanized with peroxide; EPDM with normal vulcanizing agents
Thermoplastic rubber	Block copolymer of butadiene and styrene (and many others)	Ionic “living” polymerization	High strength, excellent solvent resistance, processability
Thiokol rubber	$n\text{Na}_2\text{S} + n\text{ClCH}_2\text{CH}_2\text{Cl} \rightarrow [\text{CH}_2\text{CH}_2 - \text{S} - \text{S} - \text{S}]_n + 2n\text{NaCl}$	Step growth polymerization	Used in sealants and as a rocket fuel binder

This partly reflects the growing automobile market, but also the manufacture of high-quality acrylonitrile–butadiene–styrene (ABS) artifacts, typically casings for electronic devices, for export to the West. The “others” category for Asia-Pacific probably includes a large amount of HMDA for manufacture of nylon 66 for the huge Asia-Pacific textiles industry. The most important market for C₄s are styrene–butadiene rubber (SBR or SB rubber) and polybutadiene rubber for tires. Hence we need to summarize tire technology. Rubber technology is much older than that of the petrochemical industry, with vulcanization as an important process. We shall consider that in Chapter 8 alongside natural rubber, noting here only that vulcanization crosslinks the polymer chains in rubber, and that for this to happen the polymer chains require a proportion of double bonds.

7.1.1 Tires

A typical modern radial ply² automobile tire is not a homogeneous whole but is made up of four major components – the tread, which grips the road; the sidewall, which protects the sides of the tire, for example, from damaging collisions with the curb; the liner, which takes the place of the inner tube in a tubeless tire; and the carcass, which holds the layers together (Fig. 7.4). The tire is about 50% rubber by weight. Of this, 35% is in the tread, 35% in the carcass, 15% in the sidewall, and 15% in the liner.

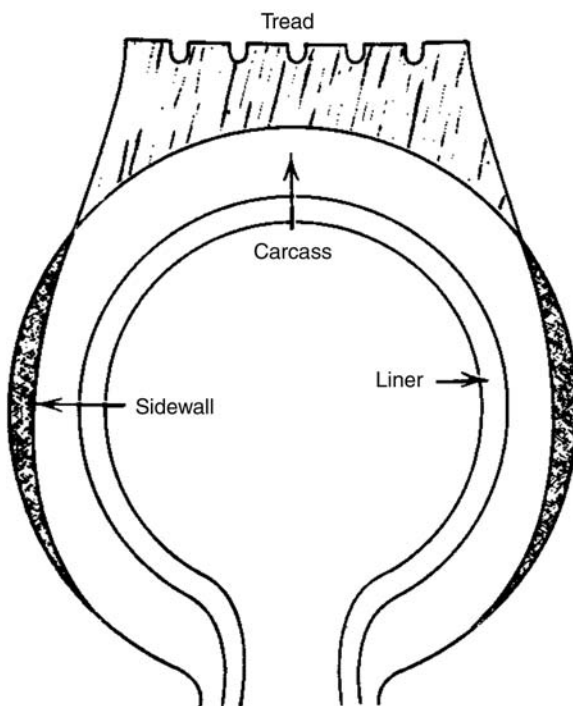


FIGURE 7.4 Profile of a typical automobile tire.

Liners are laminated onto the inside of the tire and are made of a halogenated butyl rubber/natural rubber because of the blend's impermeability to gases. Among the other components are carbon black and tire cord. The latter was traditionally rayon but polyamides and steel now predominate.

The requirement for the tires on automobiles is that they should have good wet grip, low wear, and low rolling resistance. These three are known as the magic triangle, and the improvement of one aspect is generally at the expense of the others.³ Grip is inversely related to resilience, a property at which natural rubber excels. Consequently, automobile treads contain no natural rubber and are blended from SBR and polybutadiene in an approximate 3:1 ratio. The carcass requires better flexing properties than the tread and is a natural rubber/SBR blend, with a natural rubber content greater than 60%. Sidewalls undergo continuous flexing and are a 50:50 natural rubber/polybutadiene blend.

Light trucks use tires similar to automobile tires, but the heavier the truck the larger the tire and the more natural rubber it contains. There are two reasons for increasing the content of natural rubber. First, the degree of flexing in the tire of a heavily laden truck is much higher than in an automobile, and thus more heat is generated. The larger the tire, the more difficult it is to dissipate this heat. Consequently, natural rubber is favored, because it has high resilience, low hysteresis losses, and low heat buildup. Second, grip is not as important in truck tires as in automobiles, because too rapid braking could cause disastrous shift of load. The tire tread of a medium-sized truck contains about 50% natural rubber, 30% SBR, and 20% polybutadiene plus a high proportion of natural rubber in the carcass. The tires of a heavy duty truck are entirely natural rubber. For similar reasons, aircraft tires are 100% natural rubber, while the tires on agricultural tractors, which move slowly, are made from a heavily extended SBR to minimize cost.

Premium tires are the subject of research.⁴ Replacement of the carbon black filler by high performance silicas can reduce rolling resistance by up to 25%. A nanoparticle rubber additive *Nanoprene* consists of a microgel of polymerized styrene and butadiene that has “anchor points” on its surface that bond to silica and silanes. It is to improve wear resistance and grip. Other premium tires are based on emulsion and solution styrene–butadiene rubbers and neodymium polybutadiene rubbers.⁵ The neodymium-based catalyst system produces the highest *cis* content of about 99% of all polymerization catalysts and also makes the most linear chain structure (no branching) producing a polymer with the best tensile and hysteresis (low heat buildup) properties of all the high *cis* types. Neodymium polybutadiene offers improved elasticity hence reduced rolling resistance.

7.1.2 Styrene–Butadiene Elastomers

Consumption of styrene–butadiene elastomers was static in the United States until the advent of sports utility vehicles (SUVs), which employ big tires with high rubber content. The surge in rubber consumption between 2000 and 2003, and especially of natural rubber, which is favored in larger tires, is evident from Figure 7.5. Rising gasoline prices in the United States have reversed this trend. Production of standard tires is increasingly being relocated to China, Mexico, and South America. Adding to

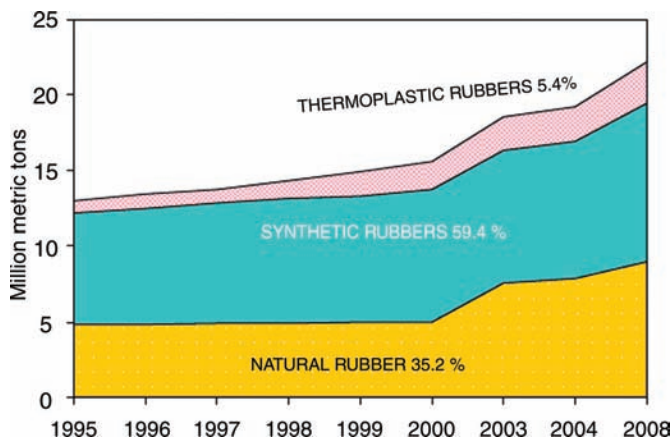


FIGURE 7.5 Global elastomer consumption.

butadiene's misfortune is the longer life of modern tires and the virtual elimination of the spare tire. Modern radial ply tires contain less SBR and more natural rubber than the older cross-ply tires. Growth in nonrubber areas, to some extent, compensates for this. Global butadiene consumption was about 6.2 million metric tons in 1990, 8.1 million metric tons in 2000, and about 9.8 million metric tons in 2009.

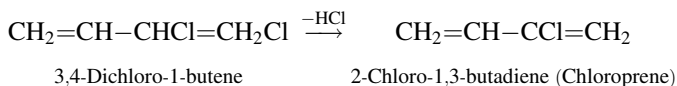
Styrene–butadiene copolymers were the original basis for latex paint, but latices with superior properties result from poly(vinyl acetate), polyacrylates, polymethacrylates, and their copolymers, and these have since captured the market. Styrene–butadiene latices are still important as coatings for paper, for carpet backing, and for caulking compounds. Styrene–butadiene block copolymers were among the first thermoplastic elastomers and are the most important. The crosslink in thermoset elastomers is covalent, created during the vulcanization process (Section 8.2.2). The crosslink in thermoplastic elastomer polymers, in contrast, is a weaker dipole or hydrogen bond. They are discussed in Section 17.3.8. A specialty butadiene–styrene block copolymer with high styrene content, one version of which is called “K-Resin,” can be blended with styrene homopolymer to increase its impact resistance. It can be used as such in adhesives and molded and extruded items, and it is stronger than polystyrene. Unlike other styrene–butadiene copolymers, “K-Resin” has the advantage of transparency.

7.1.3 Polybutadienes and Other Elastomers

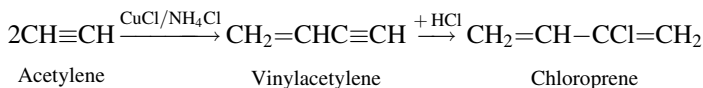
Several other synthetic rubbers are based on butadiene. The homopolymer *cis*-1,4-polybutadiene rubber, which accounts for about 28% of total U.S. usage of butadiene (Fig. 7.3), is blended with natural and other rubbers such as SBR to aid their processing and to impart resilience and reduce heat buildup in tires. It is also used in tire treads to increase wear resistance, low temperature flexibility, and resistance to aging. Two-thirds of production goes into tires and a quarter into impact modification of a wide range of resins. It is the most resilient of synthetic rubbers. Golf balls are made of it, and toy polybutadiene balls were marketed that were astonishingly bouncy.

The sophistication of modern polymerization techniques is such that it is possible to polymerize butadiene to give any of the four possible stereoisomeric forms, which vary from elastomers to hard, resinous materials (Section 17.3.10). The elastomeric form is *cis*-1,4-polybutadiene. *trans*-1,4-Polybutadiene is used in the preparation of acrylonitrile–butadiene–styrene (ABS) copolymer (Section 7.1.4). The isotactic and syndiotactic 1,2 structures are not important commercially, although syndiotactic 1,2-polybutadiene can be fabricated into photodegradable film.

The chlorination of butadiene in the vapor phase at 250°C gives a mixture of 3,4-dichloro-1-butene, $\text{CH}_2=\text{CH}-\text{CHCl}-\text{CH}_2\text{Cl}$, and 1,4-dichloro-2-butene, $\text{ClCH}_2-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$. The former may be isomerized to the latter by heat in the presence of cuprous chloride (Section 5.1.2). Dehydrochlorination of 3,4-dichloro-1-butene leads to “chloroprene,” the monomer for neoprene or polychloroprene rubbers. This use consumes about 3.7% of butadiene production.



Neoprene was an early synthetic rubber. It lacks the resilience necessary for use in tires, the major consumer of rubber, but it has good resistance to oil and ozone, which suits it for many specialized uses such as roofing and flexible hose. In the early days, it was made by reacting dimerized acetylene (i.e., vinylacetylene) with hydrogen chloride. Here is another example of petrochemicals replacing acetylene, for DuPont phased out the last acetylene-based polychloroprene plant in the United States in 1974 and in Northern Ireland in 1977.



The market for neoprene is decreasing because EP or EPDM rubbers (Table 7.2) provide longer life, especially in roofing, where they resist exposure to oxygen and ozone. The materials are also useful for making gaskets.

Nitrile rubber (Table 7.2) is a copolymer of acrylonitrile and butadiene, a typical ratio being 1:2. It is made with a redox initiator and is characterized by outstanding oil and abrasion resistance, which makes it suitable for oil seals, fuel tank fabrication, oil-resistant hoses, and ink rollers for printing presses. Dow and DSM have developed a process for dimerizing butadiene to vinylcyclohexene and subsequently styrene (Section 5.8).

7.1.4 Acrylonitrile–Butadiene–Styrene Resins

Acrylonitrile–butadiene–styrene (ABS) resins are two phase systems of styrene–butadiene rubber dispersed in a glassy styrene–acrylonitrile matrix (Section 5.8). The copolymer has the best properties if there is sufficient input of energy in the mixing to cause grafting of the rubbery and glassy phases.

ABS resins may be used between -40°C and 107°C , not a very wide temperature range but a satisfactory one. They are flammable, but fire retardants can be added. Apart from these minor drawbacks, ABS resins have excellent properties. They process reasonably, have high gloss, do not mar, and have excellent dimensional stability and good mechanical properties. In terms of price and tonnage production (6 million metric tons globally in 2009), they fit in a unique position between cheap, high volume plastics and expensive, low volume engineering plastics. They can nonetheless be described as the first of the engineering plastics.

Injection molding of ABS resins gives housings for telephones, computers, radios, business machines, pocket calculators, toilet seats, and parts for high quality refrigerators, including the doors, all essentials for 21st century life. Extrusion gives high quality pipe and fittings (the biggest use) and also sheet that is thermoformed into vehicle covers and fittings, lawn mower housings, and snowmobile shrouds. Sheet is also used for luggage and the tops of skis. And, of course, ABS resins are the raw material for the ubiquitous LEGO. In 2010, 31 billion LEGO elements (bricks or other parts) were produced. In most of the above applications, ABS is replacing metal or, in the case of telephones, phenolics and other plastics that are less impact-resistant.

ABS resins may be painted, metallized, chromium plated, or printed on and do not present the problems of a nonadhesive surface associated with the polyolefins. The plated plastic has replaced die cast metal in the radiator grilles of many automobiles. A polymer alloy of ABS with polycarbonate is used for bumpers and side panels of automobiles. ABS has nonetheless suffered from interpolymer competition from polypropylene and polycarbonate in less demanding applications.

The first commercial grades of ABS, introduced in 1948, were simply blends of a rubber with styrene–acrylonitrile (SAN) polymer. These blends reportedly used nitrile rubber since it was found to be more compatible with SAN than polybutadiene rubber. Modern ABS processes employ suspension, mass, or emulsion/mass hybrid polymerization of the three monomers: styrene, butadiene, and acrylonitrile. In these processes, an actual chemical linkage between the rubber phase and the elastomeric phase is formed. Properties of the ABS can be varied by adjusting the relative concentrations of the monomers, the degree to which the butadiene grafts to the SAN portion, or by adding an additional monomer. In general, the styrene contributes gloss and stiffness, the butadiene toughness, and the acrylonitrile temperature resistance. The largest producer of ABS in the world is Chi Mei, a relatively unknown Taiwanese company.

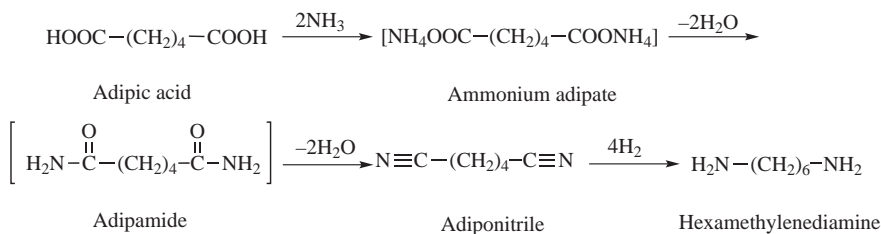
A polymer related to ABS is methyl acrylate–butadiene–styrene (MBS), produced in considerably lesser quantities than ABS. It is an impact modifier for poly(vinyl chloride) for bottles. PVC bottles are scarcely used in the United States, but in Western Europe they are used to package mineral water, cooking oil, and, to a lesser extent, alcoholic beverages. Usage of such bottles has decreased with the introduction of those based on poly(ethylene terephthalate) (Section 11.3.3).

7.1.5 Hexamethylenediamine

The remaining major application for butadiene in Figure 7.3 is hexamethylenediamine (HMDA).⁶ Only two of the various routes to HMDA start with butadiene, but

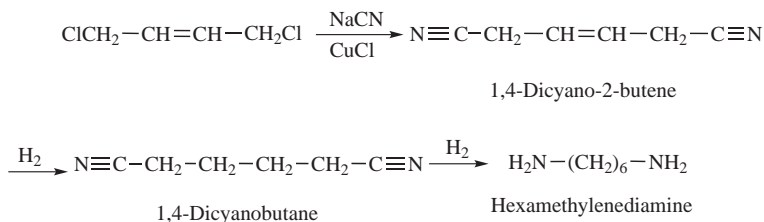
they include the most economic synthesis, and HMDA is butadiene's most important nonpolymer use. Accordingly the various routes to HMDA will be discussed here.

The evolution of syntheses for HMDA provides an excellent example of how sophisticated processes develop in the chemical industry. The first route to HMDA involved traditional reactions in which adipic acid (Section 7.2.1) and ammonia form ammonium adipate, which, on dehydration first to the amide and then to the nitrile, provide adiponitrile. This in turn may be hydrogenated to hexamethylenediamine.⁷

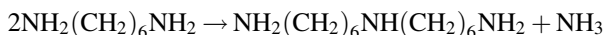


Under appropriate conditions, the reaction of adipic acid and ammonia leads to the nitrile without the isolation of intermediates. The vapor phase reaction takes place at 275°C in the presence of a mixture of boric and phosphoric acids. It may also be conducted either in the liquid phase or as a melt at a somewhat lower temperature with a phosphoric acid catalyst. Selectivity is higher in the liquid and melt phases. The synthesis is simple but has the disadvantage of starting with expensive adipic acid.

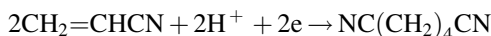
Butadiene entered the picture because of a synthesis in which a mixture of *cis*- and *trans*-1,4-dichloro-2-butenes (see above) and 3,4-dichloro-1-butene was treated with sodium cyanide to give 1,4-dicyano-2-butene. The reaction takes place at about 80°C in the presence of cuprous chloride. The 1,4-dichloro compound yields the desired 1,4-dicyano compound as might be predicted. The 3,4-dicyano-1-butene, which forms from the corresponding 3,4-dichloro compound, however, undergoes an allylic rearrangement to give more of the desired 1,4-dicyano-2-butene in both *cis* and *trans* forms at high selectivity. This is hydrogenated to adiponitrile whose nitrile groups can readily be hydrogenated to hexamethylenediamine.



Excess ammonia is used to depress formation of a triamine, which nonetheless forms in small quantities.



The electrohydrodimerization of acrylonitrile (Section 4.8) was the next synthesis. It was an ingenious departure from classical chemistry. The hydrodimerization to adiponitrile takes place by a complicated mechanism, which may be summarized as:



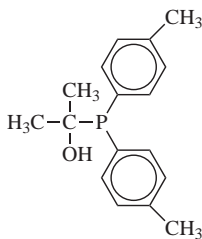
The first step is the reduction of acrylonitrile to its anion radical and this is followed by dimerization and protonation reactions. A necessary condition in the original process was the presence of a tetraalkylammonium salt as the electrolyte; otherwise propionitrile is the main product. The quaternary was thought to adsorb on the electrode to give a hydrophobic layer that prevented immediate protonation of the acrylonitrile anion radical as it was formed. A membrane to divide the cell was also required.⁸

The newest version of the process employs an undivided cell and an emulsion of acrylonitrile with 10–15% disodium hydrogen phosphate solution containing 0.4% of a complex phosphate. The aqueous phase is saturated (7%) with acrylonitrile, and the adiponitrile extracts into the organic phase as it is formed. Conversion of acrylonitrile is 50 mol % and selectivity is about 92%. By-products include propionitrile C₂H₅CN, bis(cyanoethyl) ether (NC C₂H₅)₂O, and hydroxypropionitrile HOCH₂CH₂CN. This is the only example of the use of electrochemistry to manufacture a high volume organic chemical.

Chemical means for dimerizing acrylonitrile have been studied extensively. Unlike the Monsanto process, the reaction is not a hydrodimerization. Thus it yields a mixture of the two possible 1,4-dicyanobutenes. The reaction proceeds at 1–2 bar and temperatures varying from 30°C to 100°C to give 87% conversion with a selectivity to linear products of 84%.

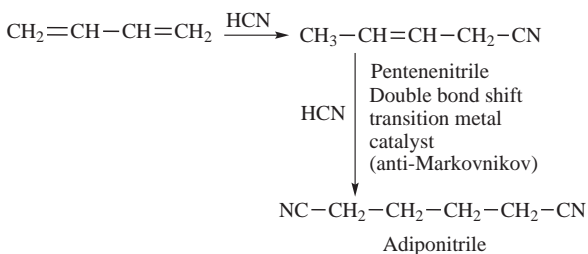


These are hydrogenated to hexamethylenediamine. A branched isomer, methyleneglutaronitrile, NC–C(CH₃)–CH₂CH₂CN, forms as a by-product and may be isomerized to a linear product. The dimerization catalysts are phosphines. 2-Hydroxyisopropyl bis-*p*-tolylphosphine is typical.



2-Hydroxyisopropyl-bis-*p*-tolylphosphine

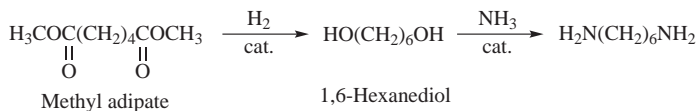
These processes are rivaled by still another process that turns out to be the most economic. It starts with the 1,4-addition of hydrogen cyanide to butadiene. The catalyst, nickel with triarylphosphite ligands, $\text{Ni}[\text{P}(\text{OAr})_3]_4$, is remarkable. It not only affects the 1,4-addition but it also isomerizes the by-product 2-methyl-3-butenitrile, which is produced in appreciable quantities, to the desired isomer. In addition, it shifts the double bond to a terminal position and then makes possible the addition of another mole of hydrogen cyanide anti-Markovnikov to the terminal bond. If it were not possible to use the same catalyst for both reactions, the double bond shift could not be carried out in high yield because of an equilibrium. The resulting adiponitrile may be hydrogenated to hexamethylenediamine.



This synthesis, as opposed to the one starting with the chlorination of butadiene, eliminates the need for costly chlorine, uses hydrogen cyanide, which is now cheaper than sodium cyanide (but not when the synthesis based on 1,4-dichloro-2-butene was devised), eliminates the handling of carcinogenic 1,4-dichloro-2-butene, and solves the problem of disposing of ecologically unacceptable copper-contaminated sodium chloride.

A simplified proposed mechanism for the HCN addition (Fig. 7.6) involves the formation of an $\text{H}-\text{M}-\text{CN}$ complex in which M is the metallic catalyst. This in turn π -bonds with the terminal olefin after which a σ -bonded complex forms, which subsequently eliminates the metal to provide the adiponitrile.

An obsolete process for hexamethylenediamine production involves the amination of 1,6-hexanediol with ammonia in the presence of Raney nickel. The diol, still manufactured for use in polyurethane formulations, results from the hydrogenolysis of methyl adipate.



Another route to 1,6-hexanediol is via cyclohexanone, which is oxidized by hydrogen peroxide or peracetic acid to caprolactone (Section 9.2.2). The lactone can then be cleaved with hydrogen in the presence of a reducing catalyst such as copper chromite to 6-hydroxycaproic acid whose ester, on hydrogenolysis, gives 1,6-hexanediol. The amination of the diol takes place in the presence of ammonia and hydrogen at 200°C and 230 bar with a Raney nickel catalyst.

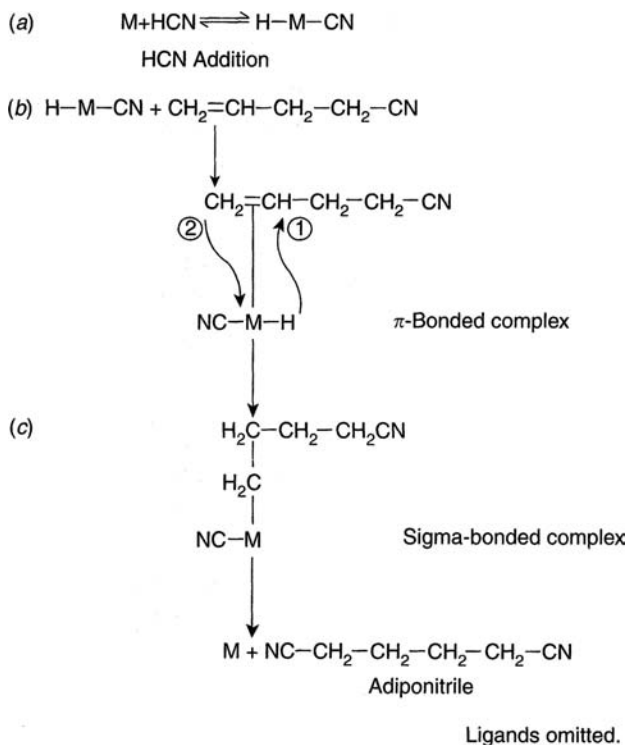
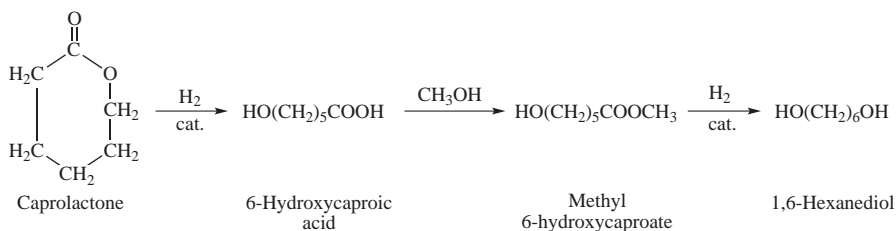
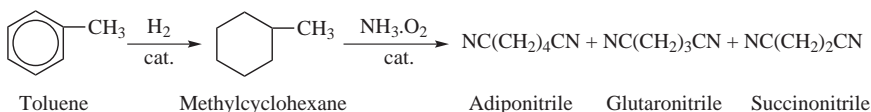


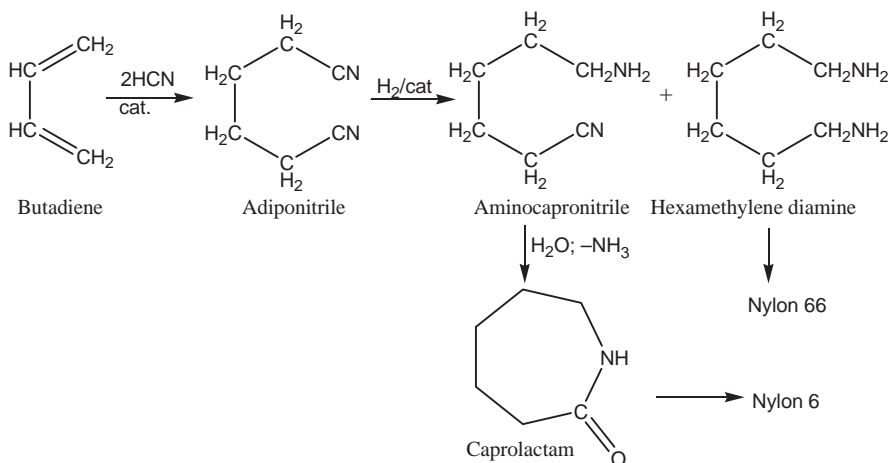
FIGURE 7.6 Mechanism of HCN addition.



A proposed process for adiponitrile, never commercialized, involves the ammoxidation (Section 4.4) of methylcyclohexane (prepared by toluene hydrogenation) at 43°C over a tin oxide–antimony oxide catalyst. Adiponitrile is produced in relatively modest yields together with by-product glutaronitrile and succinonitrile.



According to the patent literature, adiponitrile can be partially hydrogenated to a near 50/50 mixture of hexamethylenediamine and aminocapronitrile. Aminocapronitrile, which is the compound made if only one of the two nitrile groups in adiponitrile is hydrogenated, is separated from the hexamethylenediamine and is reacted with water at 240°C using a titanium dioxide catalyst. Caprolactam and ammonia are produced. This is a two-for-one process that yields monomers for both nylon 6 and nylon 66. DuPont and BASF announced their intentions to commercialize this process, but DuPont subsequently withdrew. BASF seems to be carrying on alone, although it has not announced any plans for commercialization. Other butadiene to caprolactam⁹ routes are described in Section 9.2.1.



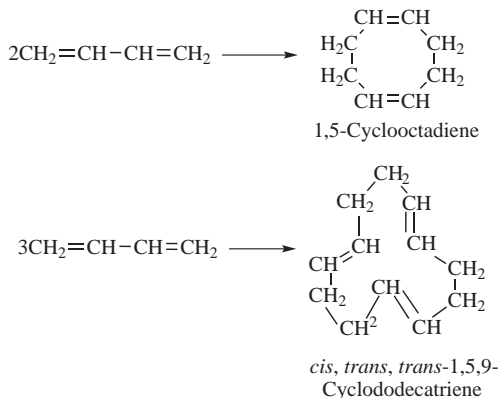
Hexamethylenediamine's major role is in the production of nylon 66 (Section 9.2.1). It can, however, be converted to an isocyanate by reaction with phosgene. This toxic product, used as a trimer to reduce its vapor pressure, is useful for the preparation of resistant, nonyellowing, glossy, low-temperature-curing coatings of which both military and civilian aircraft top coats are examples.

7.1.6 Lesser Volume Chemicals from Butadiene

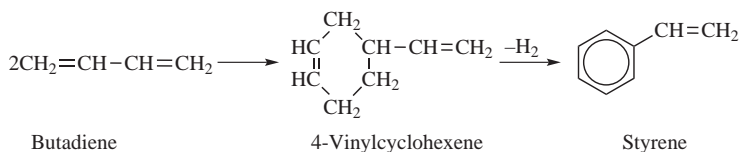
Various lesser volume chemicals based on butadiene are generated by cyclization, di- and trimerization, and the Diels–Alder reaction. Carbonylation leads to an adipic acid synthesis.

7.1.6.1 Cyclization

Cyclization of 2 and 3 moles of butadiene gives a dimer, 1,5-cyclooctadiene, and a trimer, *cis-trans-trans*-1,5,9-cyclododecatriene, an intermediate for perfumes.



Dimer formation is catalyzed by a nickel salt of 2-ethylhexanoic acid, triethylaluminum, and triphenylphosphine or triphenyl phosphite. A by-product is another butadiene dimer, 4-vinylcyclohexene, which is also produced in high yield in an uncatalyzed dimerization. It is a precursor of styrene, which forms by oxidative dehydrogenation.



This styrene process was described in Section 5.8. It has not been commercialized, although Dow described an improved catalyst in the mid-1990s.¹⁰ The catalyst with large ligands that suppresses 4-vinylcyclohexene formation is nickel in combination with *tris*-*O*-phenylphenyl phosphite. At 80°C and 1 bar, selectivity to 1,5-cyclooctadiene is 96%.

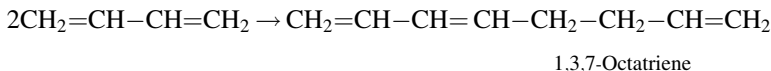
DSM has developed a related approach to styrene via butadiene. Vinylcyclohexene is dehydrogenated in the gas phase over a proprietary Pd/MgO catalyst to give ethylbenzene. The ethylbenzene can then be converted to styrene by conventional techniques.

At typical butadiene prices, both the Dow and DSM approaches are less economic than the conventional ethylene/benzene route to styrene. In addition, it would take the output from three to four steam crackers to provide enough butadiene to supply a world-class styrene plant.

Butadiene trimerizes over a titanium tetrachloride–dialkylaluminum chloride catalyst at 70°C and 1 bar to provide the *cis-trans-trans* isomer. The coproducts are minor amounts of the all *trans* isomer, polybutadiene, 1,5 cyclooctadiene, and 4-vinylcyclohexene. The *trans-trans-trans* isomer results if a nickel catalyst is used, but this is not done commercially. The catalyst is similar to the Ziegler polyethylene catalyst.

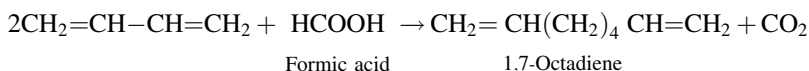
7.1.6.2 Dimerization and Trimerization

Linear dimers of butadiene are formed in several ways. One is 1,3,7-octatriene, which forms with a nickel catalyst and appropriate ligands.



More important are the products intended for hydroformylation to yield plasticizer alcohols (Section 6.9).

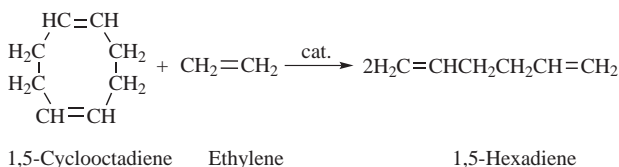
Dimers with terminal functionality, such as 1,7-octadiene, result from 2 moles of butadiene with formic acid as the source of hydrogen.



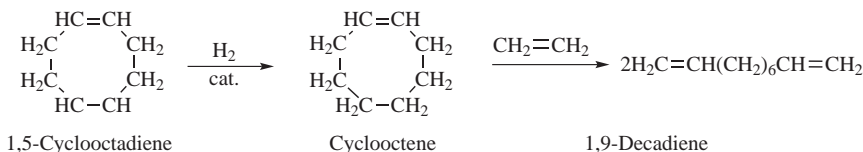
The catalyst is palladium acetate with triethylamine. The reaction is run in an aprotic solvent, dimethylformamide. Ligands such as triethylphosphine must be present. Conversion and selectivity are high, 95% and 93%, respectively.

Butadiene trimerizes over a titanium tetrachloride–dialkylaluminum chloride catalyst at 70°C and 1 bar to provide the *cis-trans-trans* isomer. The coproducts are minor amounts of the all *trans* isomer, polybutadiene, 1,5 cyclooctadiene, and 4-vinylcyclohexene. The *trans-trans-trans* isomer results if a nickel catalyst is used, but this is not done commercially. The catalyst is similar to the Ziegler polyethylene catalyst.

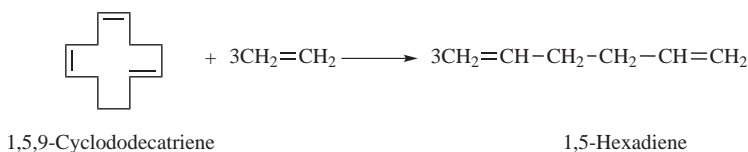
In the late 1980s Shell developed routes to two terminal olefins, 1,5-hexadiene and 1,9-decadiene. The first compound results from the metathesis (Section 4.14) of 1,5-cyclooctadiene with ethylene.



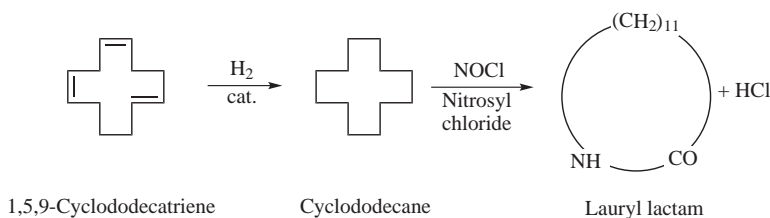
1,9-Decadiene is made by the reaction of cyclooctene with ethylene, the starting material resulting again from the selective hydrogenation of 1,5-cyclooctadiene. The heterogeneous reaction makes use of a rhenium catalyst at 5 – 20°C and 1 – 2 bar. Yields are better than 90%.



1,5-Hexadiene can also be prepared by the metathesis of 1,5,9-cyclododecatriene with 3 moles of ethylene.

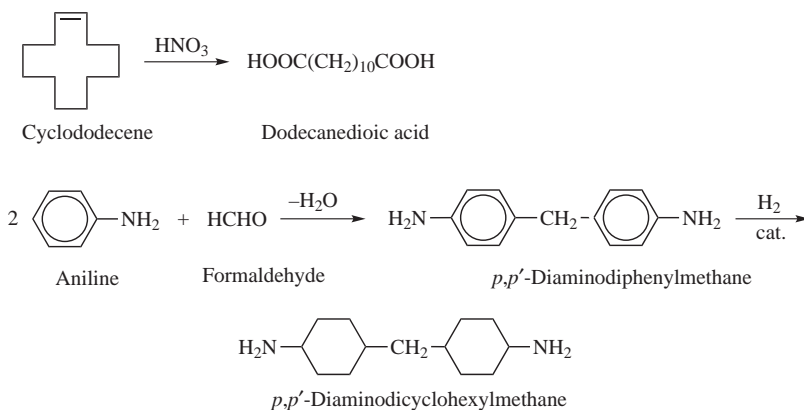


1,5,9-Cyclododecatriene can be hydrogenated to cyclododecane. Treatment with nitrosyl chloride gives laurolactam, the monomer for nylon 12.



The same process is one of several used to obtain caprolactam from cyclohexane, the monomer for nylon 6 (Section 9.2.2).

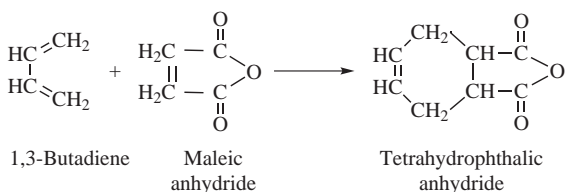
The partly hydrogenated triene, cyclododecene, can be oxidized with nitric acid to dodecanedioic acid. This was part of a now unused DuPont process to make the nylon “Qiana,” a condensate of dodecanedioic acid with bis(aminocyclohexyl)methane, which in turn was made by hydrogenation of the adduct from the condensation of aniline and formaldehyde.



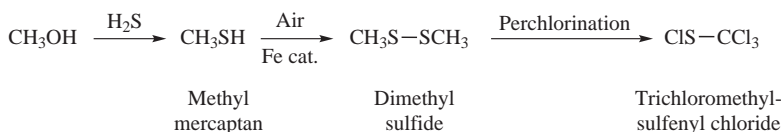
Qiana was said to have the drape and feel of silk, but still did not succeed in the marketplace, because it did not breathe and was uncomfortable to wear.

7.1.6.3 Diels–Alder Reactions

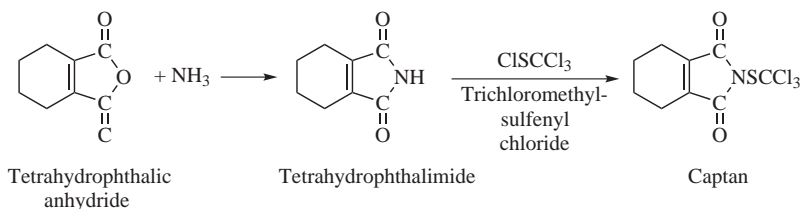
In contrast to the laboratory, the Diels–Alder condensation is used industrially only on a small scale. Nonetheless, butadiene is the classic diene for the reaction. It reacts with cyclopentadiene (Section 8.3) to give ethylidene norbornene, a monomer with two double bonds, one less reactive than the other. This is useful in EPDM rubber (Section 5.2.5). Butadiene also reacts with maleic anhydride to give tetrahydrophthalic anhydride:



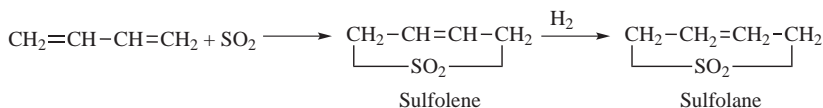
Tetrahydrophthalic anhydride is used in polyester and alkyd resins and as an ingredient in the fungicide, captan. The reagent trichloromethylsulfinyl chloride is first prepared by perchlorination of dimethyl sulfide:



This then reacts with tetrahydrophthalimide, from the reaction of ammonia and tetrahydrophthalic anhydride to yield captan:



Diels–Alder addition of sulfur dioxide to butadiene at room temperature followed by hydrogenation yields tetramethylene sulfone (Sulfolane), which is used to extract aromatic compounds (Section 4.8) from catalytic reformat in petroleum refineries.

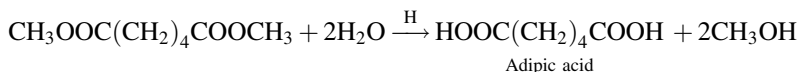
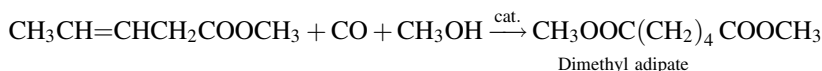


It is also mixed with diisopropanolamine and water in the so-called Sulfinol process for the removal of hydrogen sulfide, carbon dioxide, carbonyl sulfide, and other acid components from “sour” gas. The acid components are absorbed chemically by the amine and physically by the sulfolane. Being aprotic, sulfolane is also useful in extractive distillations, for example, for the separation of butadiene from other C₄ isomers.

The Diels–Alder reaction between maleic anhydride and cyclopentadiene is discussed later (Section 8.2). The Diels–Alder reaction between two molecules of butadiene yields vinylcyclohexene (Section 7.1.6.1).

7.1.6.4 Adipic Acid

Adipic acid is produced in large quantities by the classical synthesis based on cyclohexane (Section 9.2.1). It is being made by BASF in the 2000s by dicarbonylation of butadiene. This technology appears competitive with the classical route at typical butadiene costs. The reaction proceeds in two stages since the dicarbonylation is difficult. Carbon monoxide and methanol react with butadiene in the presence of dicobalt octacarbonyl in quinoline or a related base at 600 bar and 120°C to give methyl-3-pentenoate at 98% selectivity. The second step takes place at a higher temperature of 185°C but at a lower pressure of 30 bar in the presence of additional CO and methanol.



Selectivity at this point is about 85% to the desired dimethyl adipate. The migration of the double bond in the second step (cf. a similar shift in the hexamethylenediamine synthesis from butadiene, Section 7.1.5) makes possible linearity. Other catalyst systems include platinum and palladium halides, phosphines-promoted cobalt complexes, and rhodium complexes. By-products include methyl 3-pentenoate, methyl glutarate, methyl ethyl succinate, dimethyl, and diethyl succinate, and methyl pentanoates. The first two materials are obtained in largest amounts.

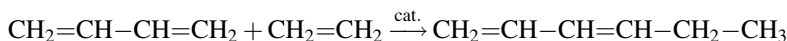
Between 1995 and 2000, DuPont/DSM, Rhone Poulenc, and Union Carbide each disclosed related work on the conversion of butadiene to adipic acid. However, no announcements of commercialization have been forthcoming.

7.1.6.5 1,4-Butanediol

Butadiene is the basis for one of the important routes to 1,4-butanediol by way of a double acetoxylation. This is described in Section 12.3.1.

7.1.6.6 *trans*-1,4-Hexadiene

trans-1,4-Hexadiene (Section 18.7.1) results from the condensation of ethylene and butadiene in the presence of a rhodium catalyst. This was the first rhodium-catalyzed homogeneous reaction to be used industrially.



The compound is a useful comonomer for the production of ethylene – propylene – diene monomer (EPDM) rubber (Table 7.2). The terminal double bond enters into the polymerization and the less reactive *trans* double bond then becomes pendant and provides a site for crosslinking or vulcanization with sulfur compounds.

7.1.6.7 Dimethyl-2,6-naphthalene Dicarboxylate

Amoco (now BP) has commercialized a process to make dimethyl-2,6-naphthalene dicarboxylate from butadiene and *o*-xylene.¹¹ This material is used as a monomer to make a specialty high temperature resistant, barrier polyester, poly(ethylene naphthalate) (PEN) (Section 11.3.3). The synthesis is shown in Figure 7.7. An alkenylation reaction over an alkali metal catalyst gives 5-(*o*-tolyl)-pentene-2, which cyclizes over a platinum and copper on zeolite catalyst to give 1,5 dimethyltetralin. Liquid phase dehydrogenation at 220–420°C and moderate pressure over platinum and rhenium on γ -alumina gives a mixture of 1,5 and 1,6-dimethylnaphthalene. The latter is separated by crystallization and the 1,5 product recycled for isomerization. Oxidation, similar to that in terephthalic acid/dimethyl terephthalate production (Section 11.3.1) gives dimethyl-2,6-naphthalene dicarboxylic acid or its dimethyl ester.

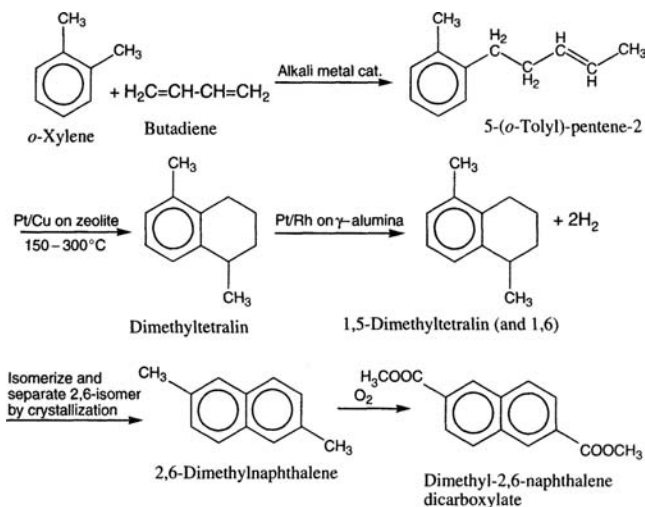
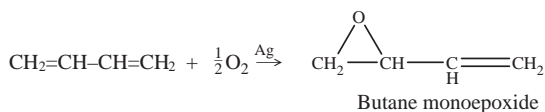


FIGURE 7.7 Synthesis of dimethyl-2,6-naphthalene dicarboxylate.

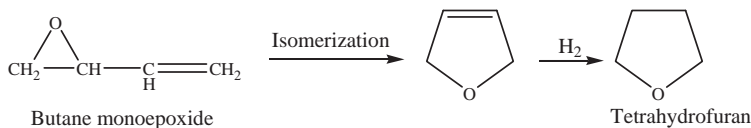
2,6-Dimethylnaphthalene is the key material in the production of the 2,6-naphthalene dicarboxylic acid and, because of the complicated multistep chemistry used in the BP Amoco process, the resulting dicarboxylate is expensive and is inhibiting the growth of poly(ethylene naphthalate); it is not clear if they still make it.

7.1.6.8 Butadiene Monoepoxide

Eastman Chemical has built a small plant to commercialize a process that converts butadiene to the corresponding monoepoxide¹²:



The chemistry is analogous to that of the silver-catalyzed direct oxidation of ethylene to ethylene oxide. Just as with ethylene, butadiene contains no allylic hydrogens and is able to undergo epoxidation smoothly to afford 3,4-epoxy-1-butene in good yield. Eastman is using this material as a convenient synthon to make a variety of specialty intermediates for the pharmaceutical and agricultural markets. This monoepoxide also has the potential to be economically converted to tetrahydrofuran for Spandex (Section 17.3.8) via the following reactions:



Although consumed on a scale almost an order of magnitude less than ethylene, butadiene has no fewer nor less interesting reactions. They are carried out, however, on a smaller scale.

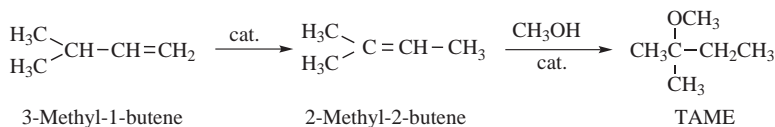
7.2 CHEMICALS AND POLYMERS FROM ISOBUTENE

Isobutene was a lackluster chemical until the 1980s. Between 1981 and 1999, however, U.S. production grew from 1.2 billion pounds to 20.9 billion pounds and peaked in 2002 (Section 4.15.1 and the beginning of this chapter). Its growth resulted from its role as a precursor for methyl-*tert*-butyl ether (MTBE), the preferred oxygen-containing additive for increasing the octane number of unleaded gasoline. As discussed earlier, MTBE use in the United States came to a halt for environmental reasons. Other uses for isobutene include formation of butyl rubber (Table 7.2, Section 7.2.2), polyisobutenes, alkylates for gasoline (Section 4.10), *tert*-butanol, methyl methacrylate (Section 6.7.1), and isoprene (Section 8.2).

A second major source of isobutene is the dehydration of the *tert*-butanol produced as a coproduct in a propylene oxide process (Section 6.4).

Because there was insufficient isobutene in the late 1980s and 1990s to satisfy the need for MTBE, processes were devised for dehydrogenating isobutane to isobutene in the same way that the butenes may be dehydrogenated to butadiene. The dehydrogenation goes more readily because isobutane has an excellent leaving group – the hydrogen on the tertiary carbon atom. The first step, the isomerization of *n*-butane to isobutane, is a well-defined refinery reaction.

A related route to octane-improving tertiary ethers is BP's Etherol process. It is intended to produce the higher analogs of MTBE by making use of the isoalkenes from catalytic cracking. These include 3-methyl-1-butene and 3-methyl-1-pentene. The catalyst, a Pd-impregnated ion exchange resin, isomerizes these to isopentene and isohexene and catalyzes the addition of methanol to the newly created, reactive double bond. Also, in the presence of hydrogen, it selectively catalyzes the hydrogenation of diolefins to monoolefins. Thus it has three functions. An example is the formation of *t*-amyl methyl ether (TAME) from 3-methyl-1-butene.



7.2.1 Methyl *tert*-Butyl Ether

The role of methyl *tert*-butyl ether (MTBE) as an octane improver in gasoline has been mentioned repeatedly. Its production and isolation directly from Raffinate I, a portion of the C₄ fraction from either steam or catalytic cracking, was discussed in Chapter 5. It can be made similarly from isolated isobutene by reaction with methanol in a highly selective reaction in the presence of an acid catalyst, usually an acidic ion exchange resin.

The phase out of MTBE presented two problems – an alternative method of enhancing octane number, and how to best revamp MTBE production equipment for alternative uses. The role of octane number enhancement is being filled by ethanol. An alternative use of equipment that is being pursued by a number of engineering contractors is to convert the MTBE etherification reactor to dimerize isobutene to diisobutenes (see below). The diisobutenes can then be hydrogenated in a new and separate reactor to give isooctane, itself a high octane gasoline component (Section 4.10) although its octane number is considerably less than that of MTBE. Isooctane production has the benefit of using the same equipment (with the addition of a hydrogenation reactor) and process conditions as for MTBE production, and it also provides an alternative use for the isobutene.

A further use for both the isobutylene and MTBE equipment is for production of ethyl *tert*-butyl ether (ETBE). ETBE is similar to MTBE in structure and process technology, with the exception that ethanol is substituted for methanol. ETBE has some advantage over MTBE in that it is higher boiling, has more energy content, has

lower affinity for water, and very importantly is partially renewable. On the downside, ETBE is more expensive than MTBE. Nevertheless, ETBE is finding some use in Western Europe and Japan because minimum levels of renewables in fuel streams have been mandated.

A potential replacement fuel additive is biobutanol, described in Section 14.5.

7.2.2 Butyl Rubber

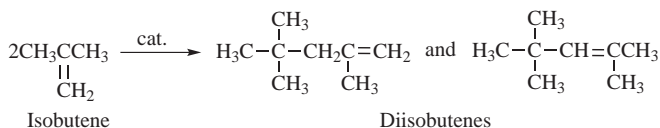
An important outlet for isobutene is in butyl rubber, a copolymer of isobutene with 2–5% of isoprene. Butyl rubber was used for inner tubes before the advent of the tubeless tire, because of its impermeability to air. The halogenated version, bromo or chlorobutyl rubber, is used as an inner liner for tubeless tires, for truck inner tubes, for tire sidewall components, and for air cushions and bellows. Without the isoprene, the polymer would contain no double bonds and would not vulcanize with sulfur. The isoprene comonomer leaves only a small number of double bonds to be crosslinked and the resulting polymer contains little if any unsaturation. For this reason, it resists aging and is therefore useful in constructions such as tops for convertibles.

7.2.3 Polyisobutenes and Isobutene Oligomers and Polymers

Isobutene can be polymerized to polyisobutene under the influence of Friedel–Crafts catalysts such as boron trifluoride or aluminum chloride. The lower molecular weight liquid products are adhesives and tackifiers. The higher molecular weight products are used in caulking compounds and as a chewing gum base.

Oligomeric polybutenes are made by polymerizing Raffinate I with an acid catalyst such as aluminum chloride and with hydrochloric acid as an activator. The *n*-butenes act largely as chain stoppers since the isobutene polymerizes much more rapidly. The resulting low molecular weight (1000–1500) oligomers, functionalized by reaction with maleic anhydride, are used as additives for lubricating oils and gasoline.

Like propylene and the butenes, isobutene is used for alkylates for gasoline and it may be dimerized or oligomerized to give diisobutenes, unsaturated precursors of 2,2,4-trimethylpentane. Both the unsaturated and subsequently hydrogenated compounds increase the octane number of gasoline, the latter, of course, being more stable. This reaction has become more significant because of the MTBE phase-out.



The diisobutenes may be hydroformylated (Section 6.9) to branched chain aldehydes, which can be hydrogenated to branched nonanol. Alkylation of phenol with nonanol gives nonylphenol, which can subsequently be ethoxylated to give nonionic surfactants. Diisobutenes are also used to alkylate phenol directly to provide branched chain

octylphenol also for the preparation of ethoxylated nonionic surfactants. The octyl compound is used on a much smaller scale but, in spite of conflicting claims, both are likely to be phased out because of their lack of biodegradability.

7.2.4 *tert*-Butanol

Isobutene may be hydrated to *tert*-butanol with an acid catalyst such as 60% sulfuric acid at a low temperature of 10–30°C with very high selectivity and yield. This is the major route for isolating isobutene from Raffinate I. *tert*-Butanol is also produced concurrently with propylene oxide as described in Section 6.8. A third route is acidification of *tert*-butyl hydroperoxide, which in turn results from the reaction of isobutane with oxygen. This is not done commercially since the major interest in *tert*-butanol has been for dehydration to isobutene that is also readily obtained by isobutane dehydrogenation. The dehydrogenation is more difficult than the dehydration, but most isobutene for MTBE still came from isobutene because there was not enough *tert*-butanol.

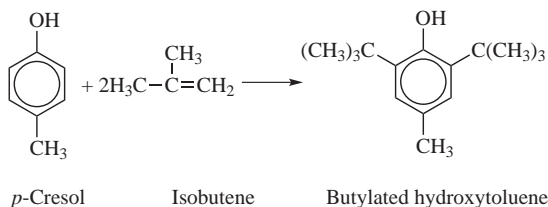
tert-Butanol is a solid that dissolves readily in gasoline and has been used as an octane improver. It may be mixed with an equal quantity of methanol, which by itself is not useful in gasoline because it separates out as a second layer in the presence of moisture. However, neither the *tert*-butanol nor the methanol-*tert*-butanol combination is as effective as MTBE. The fate of most *tert*-butanol is its dehydration to isobutene, which is done in the refinery in the separation of C₄s and as a step in methyl methacrylate production in Japan.

7.2.5 Methyl Methacrylate

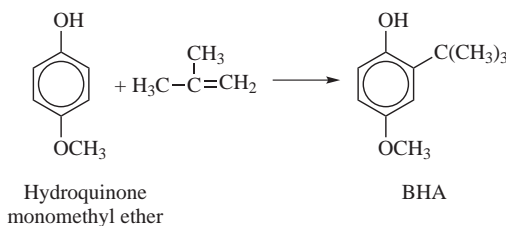
Both isobutene and *tert*-butanol can be oxidized to methacrylic acid (Section 6.7.1). Methacrylaldehyde is an intermediate. Both undergo ammoxidation to methacrylonitrile, an intermediate for the preparation of methacrylic acid in one Japanese process that is not currently in use.

7.2.6 Lesser Volume Chemicals from Isobutene

Two small volume but widely used products based on isobutene are butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). BHT results from the interaction of isobutene and *p*-cresol with a silica catalyst.

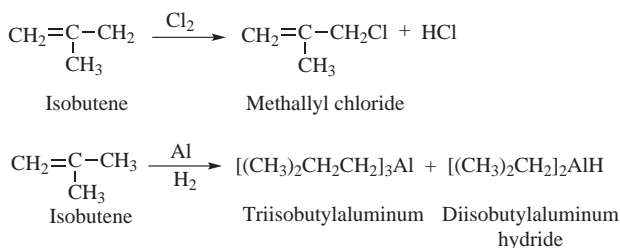


BHA results from the reaction of 1 mole of isobutene with the monomethyl ether of hydroquinone.

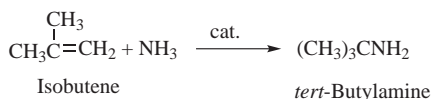


BHT and BHA are oil-soluble antioxidants for rubbers and plastics and for fatty foods such as shortenings. Small quantities protect huge tonnages of products as diverse as elastomers and shortening from deterioration and thus have great economic significance. The food usage has been investigated repeatedly by the U.S. Food and Drug Administration but thus far no evidence against them has been found. Even so, their use in food products is decreasing.

Liquid phase chlorination of isobutene at 400–500°C leads to methallyl chloride (cf. allyl chloride, Section 6.11.1). Treatment with aluminum and hydrogen gives triisobutyl aluminum and diisobutyl aluminum hydride, both important as Ziegler–Natta polymerization catalysts. The hydride is also a reducing agent.

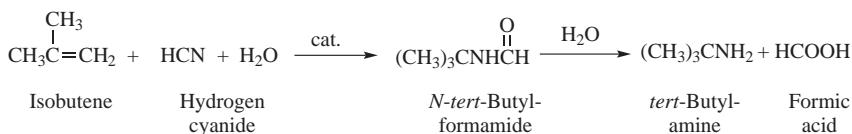


Isobutene figures prominently in a synthesis of isoprene as discussed in Section 8.1. Isobutene and ammonia yield *tert*-butylamine with a catalyst of ammonium iodide promoted with chromium chloride.

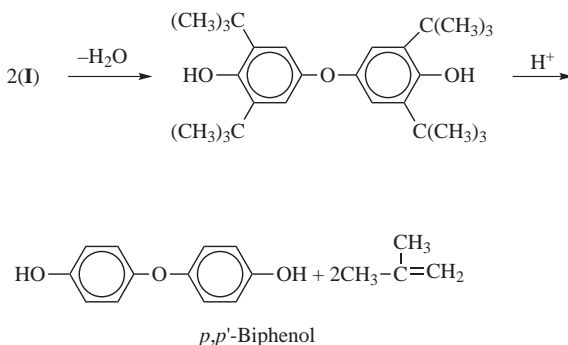
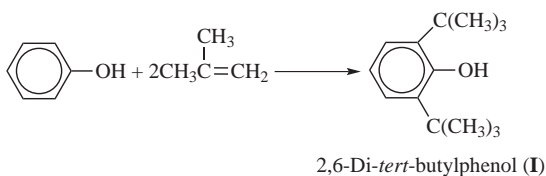


Conversion is 19% at 100% selectivity. The reaction is probably not yet used industrially. This is a demonstration of the high reactivity of the double bond of isobutene, since ammonia addition to a double bond normally takes place only with difficulty and with specialized homogeneous catalysts. *tert*-Butylamine is normally made by the Ritter reaction of isobutene with hydrogen cyanide, which involves the

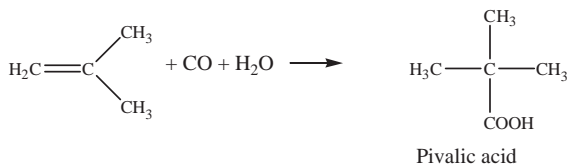
addition of hydrogen cyanide and water to a double bond, followed by in situ hydrolysis of the resultant formamide.



tert-Butylamine is used in the formulation of lubricating oil additives. The labile nature of the *tert*-butyl group makes isobutene valuable in chemical synthesis. An example is the use of isobutene as a shielding group for the synthesis of *p,p'*-biphenol, a monomer for liquid crystal polymers. Phenol is alkylated with isobutene to give 2,6-di-*tert*-butylphenol. Two moles can then be coupled in the *para* position to give a diquinone, which can be hydrogenated to the substituted biphenol. The protective *tert*-butyl groups can be removed by acid catalysis and the recovered isobutene can be recycled.



Hydrocarboxylation of isobutene via the Koch reaction gives pivalic acid:



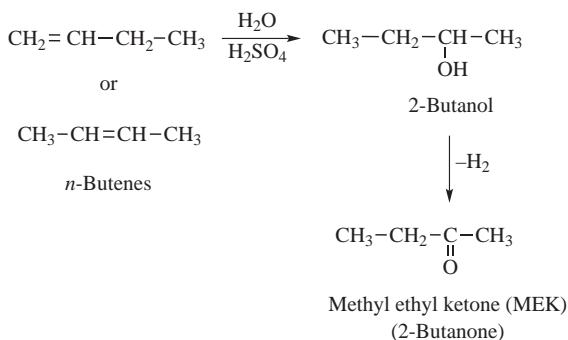
The reaction is catalyzed by hydrogen fluoride. Isobutanol or *t*-butanol can be used instead of isobutene. Pivalic acid is the simplest member of a class of acids known as Koch acids. They are characterized by a tertiary carbon attached to a carboxyl group, and are known as “neoacids” or “VersaticTM” acids. The two largest producers are ExxonMobil and Hexion (formerly Shell). Pivalic acid is an intermediate for the production of specialty organic peroxides, agrochemicals, and pharmaceuticals. Glycidyl esters of pivalic acid are finding increasing use in coatings formulations, while vinyl esters find application as specialty monomers. The global market is on the order on several thousand tons.

7.3 CHEMICALS AND POLYMERS FROM 1- AND 2-BUTENES

Most uses for the butenes are relatively low volume. Pure 1-butene plays an important role in the production of linear low density polyethylene and to a lesser extent of high density polyethylene (Sections 5.1.3 and 5.1.4). Global demand for 1-butene is about one million metric tons per year.

In combination with isobutene, the mixture of 1-and 2-butenes is polymerized to so-called polybutenes (Section 7.2.3). 1-Butene can be polymerized to poly(1-butene) with a Ziegler–Natta catalyst. Like the polypropylene of commerce (Section 4.1), it has an isotactic structure. Its advantages over polypropylene are that it is less prone to stress cracking and has high temperature tensile strength and less cold flow. Its major use, which is small, is in construction of pipes and vessels for handling and storing corrosive liquids at high temperatures and pressures. It is not useful in molding because of postcrystallization, which leads to shrinking.

Like propylene and isobutene, 1-butene and 2-butene mixtures can be hydrated with concentrated sulfuric acid to give 2-butanol.



Direct hydration, as with ethylene and propylene, is also possible (Section 5.9). *sec*-Butanol has a few minor uses as a solvent, but most if it is dehydrogenated to methyl ethyl ketone (MEK), an important solvent for vinyl and nitrocellulose lacquers and acrylic resins. In the United States, a vapor phase process with a zinc oxide or zinc–copper catalyst is used, while in Europe a liquid phase reaction with finely divided nickel or copper chromite is preferred.

The mixture of 1- and 2-butenes (Raffinate II) can also undergo the oxo reaction to give a mixture of pentanals and, more important, amyl alcohols. With the latest generation of oxo catalysts (bisphosphite-modified rhodium), hydroformylation of Raffinate II gives *n*-valeraldehyde as the major product. Valeraldehyde can be converted to 2-propylheptanol, a C₁₀ plasticizer range alcohol. Alternatively, the Raffinate II can be dimerized to mixed octenes using IFP's (now Axens') Dimersol X process (Section 6.3) and then converted to C₉ plasticizer range alcohols via oxo chemistry (Section 6.9). The amyl alcohols are useful as solvents as such or as their esters. As described previously, catalysts are available that lead to a high percentage of *n*-amyl alcohol from 1-butene.

Like propylene, 1- and 2-butenes have uses in gasoline, for they may be alkylated with isobutane to provide branched chain structures. Indeed, they are preferred to propylene for alkylate because they provide more highly branched molecules. They also may be components of polygas. If the oligomerization takes place with propylene, heptenes are produced, which can be used as the basis for C₈ oxo alcohols (Section 4.9).

2-Butene is the starting material for a process, as yet uncommercialized, for isoprene (Section 8.2). Also, it undergoes metathesis with ethylene to give propylene. This "on-purpose" route to propylene is discussed in Section 6.1.

A small amount of 1-butene is converted to butene oxide presumably by epoxidation with a peracid. Like isobutene, it forms aluminum derivatives such as tributylaluminum, a useful Ziegler–Natta catalyst.

1- and 2-Butenes may be dehydrogenated to butadiene (Section 7.1) at a temperature of 650°C in the presence of steam, which not only minimizes butadiene polymerization but also inhibits carbon deposition on the catalyst. The dehydrogenation is endothermic and thus a pressure of 0 – 1 bar is used at a contact time of 0.2 second. The catalyst comprises calcium nickel phosphate. Oxidative dehydrogenation is also possible and is in fact preferred since it makes possible operation at lower temperatures of around 550°C with a fixed catalyst bed. The hydrogen released reacts with oxygen to form water, an exothermic reaction that compensates for the heat lost by the endothermic dehydrogenation.

7.4 CHEMICALS FROM *n*-BUTANE

7.4.1 Acetic Acid

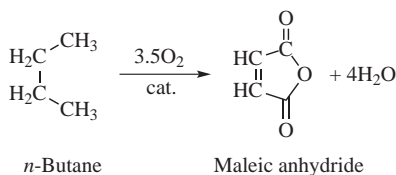
One of the earliest routes to acetic acid was based on the liquid phase oxidation of hydrocarbons such as *n*-butane and light naphtha. This process is discussed in Section 12.5.2.2.

7.4.2 Maleic Anhydride

1- and 2-Butenes may be oxidized to maleic anhydride analogously to the oxidation of propylene to acrylic acid (Section 6.4), the 1-butene isomerizing to the more

thermodynamically stable 2-butene. The original catalyst was vanadium pentoxide. Maleic anhydride traditionally has been prepared by the oxidation of benzene over the same catalyst (Section 9.5). A benzene shortage in the early 1970s motivated the development of an alternate route based on butenes, and the new route also had the advantage that two carbon atoms were not lost. *n*-Butenes are not as important for refinery reactions in Europe as they are in the United States and therefore are not much more expensive than *n*-butane.

n-Butane, cheaper in the United States, was investigated as a feedstock for maleic anhydride and unexpectedly proved adequate. It was an early and successful example of alkane functionalization, a topic discussed in more detail in Chapter 13.



The pathway for the oxidation of 2-butene to maleic anhydride is analogous to the oxidation of propane to acrylic acid, but there is no analogous reaction involving the oxidation of a saturated hydrocarbon in reasonably high selectivity, with only carbon dioxide and water as by-products. The oxidation of *n*-butane or naphtha to acetic acid (Section 12.5.2.2) is not analogous because numerous by-products are produced.

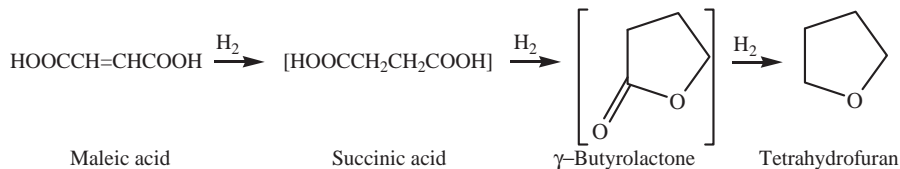
It is impressive that a catalyst system can be found that will oxidize methyl groups to carboxyls and insert a double bond while refraining from promoting C—C bonds scission. The reason is that maleic anhydride, with its conjugated double bond system, is remarkably stable. The formation of an activated complex through which further oxidation could take place involves disruption of this conjugation and hence has a high activation energy.

By the early 1980s, *n*-butane oxidation had become the preferred method for maleic anhydride manufacture. The reaction may be carried out either in a fixed or fluid bed reactor, the latter requiring an attrition-resistant catalyst. The secondary products, as in ethylene oxidation to ethylene oxide (Section 5.7), are carbon dioxide and water. The fluidized bed reaction, instituted in Japan in the early 1990s, is carried out with a butane concentration in air of 4.5% at a temperature of 440°C with a contact time of about 11 seconds. The catalyst is based on vanadium pentoxide and various phosphoric acids. Other catalysts described in the patent literature contain boron, lithium, and zinc as activators.

Butane-based maleic anhydride processes are conventionally carried out without hydrocarbon recycle and thus maximum yield, not selectivity, is important. The nitrogen in air complicates recycle loops but, because no recycle is employed in this process, air can be used as the oxidant rather than expensive oxygen. Typical selectivities range from 50% to 52%. In the late 1990s, DuPont developed a process to make maleic anhydride by a so-called transport bed. In this approach, DuPont first oxidized a specially formulated catalyst in a reactor with air, and then in a second

reactor butane was oxidized to maleic anhydride with the activated catalyst. The depleted catalyst was then reoxidized and the process started all over again.

The plant was built by DuPont in Spain as part of a larger complex to make tetrahydrofuran for Spandex production. They hydrolyzed the maleic anhydride product to give aqueous maleic acid. This was subjected to hydrogenolysis to yield tetrahydrofuran (Section 12.3.1) with a newly developed catalyst that made possible the use of milder temperatures and pressures than are commonly required for hydrogenolyses.



DuPont required tetrahydrofuran for oligomerization to a polybutene ether for use in their Spandex polymer. Spandex is a block copolymer comprising hard urethane blocks and flexible polyether blocks, useful for hosiery, swimsuits, sports clothes, and elastic in undergarments. Although it is an old polymer, its use increased rapidly in the late 1980s and early 1990s when pantyhose and tights became fashionable. However, DuPont shut down this plant after only a few years of operation as the process was plagued with technical problems. Soon after, they sold their fiber businesses, named Invista, to Koch Industries.

Maleic anhydride consumption in the United States in 2008 was 251,000 metric tons (Fig. 7.8). It finds its greatest market in unsaturated polyester resins

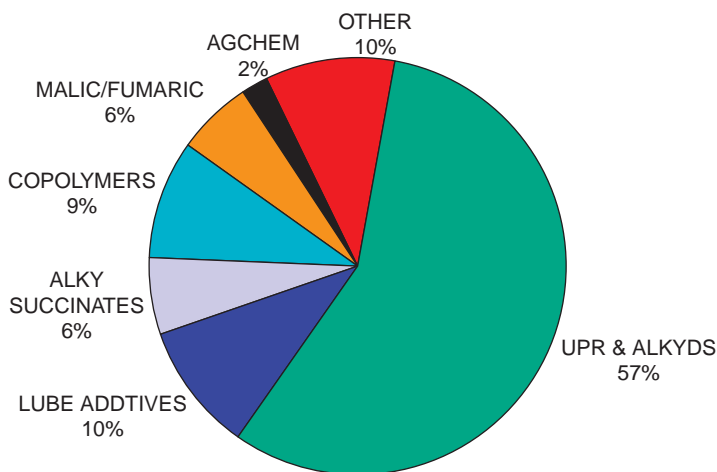
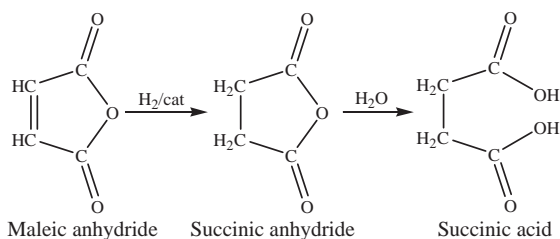


FIGURE 7.8 Maleic anhydride end-use pattern, United States 2008. Total consumption 251,000 metric tons. UPR = unsaturated polyester resin. “Others” includes polyaspartic acid and tetrahydrophthalic anhydride.

(Section 11.1.3). Other important uses are conversion to fumaric acid for use as a food acidulant and in the formulation of agricultural chemicals and lube oil additives. Its newest use is for conversion to 1,4-butanediol (Section 12.3.1).

7.4.3 Succinic, Malic, Fumaric, and Tartaric Acids

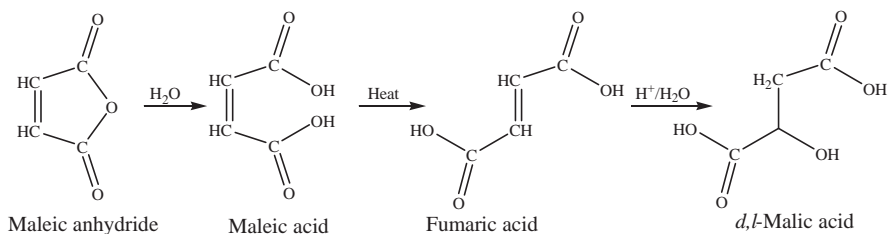
Succinic acid used to be made from maleic anhydride or as a by-product from the few remaining butane or primary flash distillate acetic acid plants (Section 12.5.2.2). The maleic anhydride route involves catalytic hydrogenation to succinic anhydride followed by hydration to the acid:



Production in 2009 was a mere 30,000 metric tons per year but is predicted to rise to 180,000 tons by 2015 as a result of the introduction of biosuccinic acid (Section 16.5).

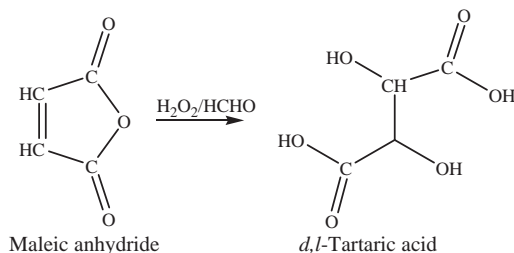
DSM and Roquette are planning to bring a glucose-based biosuccinic acid plant on stream in 2011. Bioamber is also building a glucose-based biosuccinic acid plant using a modified *Escherichia coli* organism. They have added a novel, water-based downstream purification process.¹³

Hydration of maleic anhydride gives maleic acid, which, on heating with water, isomerizes to fumaric acid, used as an acidulant and meat tenderizer and also in unsaturated polyester resins and alkyd resins. Acid-catalyzed hydration of fumaric acid gives *d,l*-malic acid, which competes with citric acid as an acidulant in soft drinks.



Reaction of maleic anhydride with formic acid/hydrogen peroxide gives tartaric acid. Tartaric acid is also a by-product of the wine industry and its salts are used in some

baking powders, dyeing operations, and piezoelectric devices and as a silver reducing agent in traditional mirror manufacture.



ENDNOTES

1. This topic is reviewed in Nexant ChemSystems PERP report 99/00S13, *Chemicals from Butadiene* (January 2001) and PERP report 01/02-3, *Butadiene/Butylenes* (February 2003).
2. The difference between the traditional cross-ply and modern radial ply tires is described in H. A. Wittcoff and B. G. Reuben, *Industrial Organic Chemicals in Perspective*, Vol. 2, p.138, Hoboken, NJ: Wiley, 1980, and in Wikipedia, http://en.wikipedia.org/wiki/Radial_tire.
3. <http://www.specialchem4polymers.com/resources/latest/displaynews.aspx?id=3075>.
4. N. Eisberg, *Chem. Ind.*, 11 February 2008, pp. 21–23.
5. <http://www.iisrp.com/WebPolymers/01FinalPolybutadieneVer2.pdf>.
6. H. A. Wittcoff, *J. Chem. Ed.*, **56**, 654, 1979.
7. Rhone-Poulenc's work on converting butadiene to adipic acid is described in U.S. Patents 5,625,096 (29 April 1997) and 5,312,979 (17 May 1994). Butadiene-based approaches to adipic acid are described in joint patents to DuPont and DSM, European Patent 0 662 467B1 (6 May 1998) and U.S. Patents 5,710,325 (20 January 1998) and 5,840,959 (24 November 1998).
8. The dimerization of acrylonitrile is described in *Chem. Week*, 7 March 1990, p. 9, in European Patent Publication 0352007A2 (24 January 1990), and in U.S. Patent 4,958,042 (18 September 1990).
9. Patents describing the coproduction of caprolactam and HMDA include U.S. Patents 5,151,543 (29 September 1992) to DuPont and 5,496,941 (5 March 1996) to BASF and World Patent 96/20931 (11 July 1996) to BASF.
10. U.S. Patents 5,196,621 (23 March 1993) and 5,329,057 (12 July 1994) and World Patent 94/01385 (20 January 1994), all to Dow Chemical Co.
11. U.S. Patents 4,990,717 (5 February 1991), 5,073,670 (17 December 1991), and 5,510,563 (23 April 1996).
12. U.S. Patents 5,362,890 (8 November 1994) and 5,312,981 (17 May 1994) both to Eastman Chemical.
13. <http://www.in-pharmatechnologist.com/Materials-Formulation/Bio-succinic-acid-to-go-commercial>; <http://www.epa.gov/greenchemistry/pubs/pgcc/winners/sball.html>.

CHAPTER 8

Chemicals from the C₅ Stream

The C₅ olefins are not a major source of chemicals and global demand is estimated at less than two million metric tons. Demand for isoamylenes (a mixture of 2-methyl-2-butene and 2-methyl-1-butene also known as isopentenenes) for conversion to the octane improver *tert*-amyl methyl ether (TAME) was expected to increase, but with the demise of MTBE (Section 7.2.1), the death of similar fuel oxygenates such as TAME was also virtually assured.

Like propylene and the C₄ olefins, the C₅ olefins are produced by both catalytic and steam cracking (Sections 4.5.1 and 4.6) of liquid feedstocks. Just as catalytic cracking produces butenes but no butadiene, it produces pentenes but practically no diolefins such as isoprene and cyclopentadiene. The steam cracking of naphtha or gas oil, on the other hand, produces isoprene equivalent to 2.5% of the ethylene formed. The C₅ fraction from gas oil cracking as well as from high temperature naphtha cracking contains more cyclopentadiene (15–25%) than isoprene, which is present to the extent of 10–15%. The former is formed by the temperature-induced cyclization of the latter. From naphtha cracked at lower temperatures, consequently, there is more isoprene than cyclopentadiene.

Steam cracking of liquids produces a fraction called pyrolysis gasoline, which contains both the C₅ olefins and an aromatic fraction. It may all be sent to the gasoline pool, usually after hydrogenation of the double bonds. Alternatively, the C₅ fraction is recovered by distillation, and the remainder hydrotreated to remove any remaining olefins. After this it is processed like catalytic reformat (Section 4.8) to remove benzene and toluene. The residue is then sent to the gasoline pool.

Since the United States has cracked ethane and propane predominantly, pyrolysis gasoline has not been a major source of C₅ olefins. The Chinese, like the Europeans, crack heavier feeds, which produces relatively greater amounts of C₅ olefins. They have therefore been developing a more extensive C₅ olefin industry as a way to add value to their steam crackers.

The number of hydrocarbon isomers increases with increasing chain length. There is only one C₂H₆ and one C₃H₈ hydrocarbon but two C₄H₁₀ compounds and three C₅H₁₂ isomers. In the C₅ steam cracking fraction, there are appreciable quantities of thirteen components as shown in Figure 8.1, and others can be written but are present in negligible quantities. Of the isomers present, isoprene and cyclopentadiene are isolated as pure compounds.

The isopentenenes (methylbutenes) are isolated as mixed isomers. One use is dehydrogenation to isoprene. Isopentane can also be dehydrogenated to isoprene, and this is believed to be done in the CIS. Synthetic natural rubber (an oxymoron, meaning polyisoprene made from petrochemical feedstocks) is more important there than in the United States. For dehydrogenation, the olefin–alkane mixture can be used, the olefin dehydrogenating first. In the United States, the 3-methyl-1-butene is



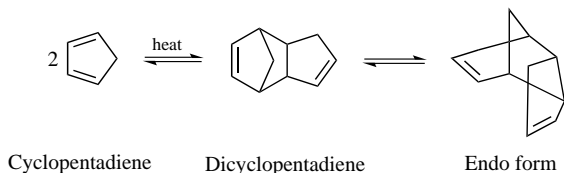
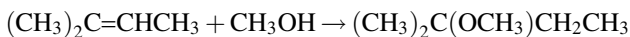
Compound	Typical Composition (%)	Carbon skeleton
<i>n</i> -Pentane	21.2	$\text{C}-\text{C}-\text{C}-\text{C}-\text{C}$
Isopentane (Methylbutane)		$\begin{array}{c} \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$
<i>n</i> -Pentenenes	5.6	$\text{C}-\text{C}-\text{C}=\text{C}-\text{C}, \text{C}-\text{C}=\text{C}-\text{C}-\text{C}$ (<i>Cis</i>) $\text{C}-\text{C}=\text{C}-\text{C}-\text{C}$ (<i>Trans</i>)
Isopentenenes	12.6	$\begin{array}{c} \text{C}-\text{C}=\text{C}-\text{C}, \\ \\ \text{C} \end{array}$ 2-methyl-2-butene $\begin{array}{c} \text{C}=\text{C}-\text{C}-\text{C}, \\ \\ \text{C} \end{array}$ 2-methyl-1-butene $\begin{array}{c} \text{C}-\text{C}-\text{C}=\text{C} \\ \\ \text{C} \end{array}$ 3-methyl-1-butene
Isoprene	19.5	$\begin{array}{c} \text{C}=\text{C}-\text{C}=\text{C} \\ \\ \text{C} \end{array}$
Cyclopentane	4.6	
Cyclopentadiene	21.5	
Pentadienes	13.7	$\text{C}=\text{C}-\text{C}=\text{C}-\text{C},$ Piperlyene $\text{C}-\text{C}=\text{C}=\text{C}-\text{C},$ 2,3 Pentadiene

FIGURE 8.1 Components of the C₅ fraction and typical composition of standard severity steam cracking of naphtha C₅ stream (remaining balance of 1–3% is C₆+).



Isoprene is removed next, by extractive distillation with an aprotic solvent such as acetonitrile or *N*-methylpyrrolidone. Almost all the alkanes and most of the olefins distill overhead, while the solvent, the diolefins, and the C₅ acetylenes appear at the bottom of the column. Successive distillations of this bottom stream regenerate the solvent for recycle, split the hydrocarbon stream into acetylenes and diolefins, and split the diolefins into isoprene and piperylene (1,3-pentadiene). Polymerization grade isoprene requires a further distillation for adequate purification.

The overhead stream from the extractive distillation can be further distilled to give 1-pentene, isopentenenes (methylbutenes), and a mixture of the remaining C₅ alkanes and olefins. The isopentenenes, mainly 3-methyl-1-butene, are isomerized by 65% sulfuric acid primarily to 2-methyl-2-butene (CH₃)₂C=CHCH₃, and to a lesser extent to 2-methyl-1-butene, CH₂=C(CH₃)CHCH₃. These react readily with water in the presence of sulfuric acid at 0–10°C to yield a tertiary alcohol, 2-methyl-2-butanol, just as isobutene does in the process for separating the C₄ olefins (Chapter 7). The 2-methyl-2-butanol is separated and heated to 350°C to regenerate the alkene. The methylbutanol can be dehydrogenated to isoprene with a catalyst based on iron, chromium oxides, and potassium carbonate at 60°C. Selectivity is 85% at 35% conversion. Just as with isobutene, methanol may be used instead of water (Section 7.2.1). With 2-methyl-2-butene, *tert*-amyl methyl ether (TAME) results (Section 7.2).



The residual C₅ stream contains linear and mixed olefins. They can be separated without difficulty but there is little demand for them. The mixture can be polymerized to give an inexpensive hydrocarbon resin (Section 8.3) useful in coatings and adhesives.

ExxonMobil Chemical developed a catalyst that could crack TAME to give isoamylenes (a mixture of 2-methyl-2-butene and 2-methyl-1-butene) and methanol. This reaction is a convenient way to separate isoamylenes from other close boiling C₅ olefin components. The 2-methyl-1-butene can be isomerized to desired 2-methyl-2-butene. ExxonMobil Chemical is believed to use these techniques to extract pure high purity 2-methyl-2-butene for use in tackifier resins.

8.2 ISOPRENE

8.2.1 Natural Rubber

Isoprene is 2-methyl-1,3-butadiene, CH₂=C(CH₃)CH=CH₂. Natural rubber is *cis*-1,4-polyisoprene (Table 7.2). It is secreted by the Para rubber tree, *Hevea brasiliensis*, and

remained a curiosity until, in 1823, Charles Mackintosh invented a method of waterproofing cotton with a solution of rubber in naphtha. It had many disadvantages, being soft and tacky when warm but rigid when chilled. In 1839, Charles Goodyear, an American inventor, showed that, when heated with sulfur, rubber becomes harder, tougher, and less sensitive to temperature changes. The process became known as vulcanization, and the properties of the vulcanized rubber could be altered by varying the amount of sulfur incorporated. Thirty to forty percent sulfur gives a hard compound, which bears little resemblance to conventional elastomers. It is known as ebonite. It is often used in bowling balls, smoking pipe mouthpieces, pen bodies, and musical instrument mouthpieces. Until the advent of modern plastics, it was used for the cases of automobile batteries.

The tapping of rubber from wild rubber trees under atrocious conditions (for the natives) made the entrepreneurial inhabitants of Manaus, Brazil, very rich until an Englishman, H. A. Wickham, smuggled 70,000 rubber tree seeds out of Brazil in 1876. The seedlings were germinated at Kew Gardens, London, and sent to Ceylon and Malay to form the basis of the plantation rubber industry. The wild rubber industry collapsed just when the advent of the automobile hugely increased the demand for rubber.

Less well known is that in southern Mexico and northern Central America the Olmecs were vulcanizing or curing rubber as early as the second millennium B.C. Subsequently, the Mayas and later the Aztecs took on this technology. When Cortez came to Mexico he was startled to see the natives playing a complex ball game with a solid rubber ball 8 inches in diameter. The ball bounced many feet into the air. The rubber was apparently cured by the juice of a morning glory vine that wrapped itself around the rubber tree. How convenient of nature that it placed the two components in such proximity. The critical components in the juice are apparently not clearly defined but traces of sulfonic acids and sulfonyl chlorides are present.²

8.2.2 Vulcanization

The vulcanization process involves the formation of crosslinks between the double bonds in the polyisoprene chains (Fig. 8.3). The number of sulfur atoms in the crosslinks varies between one and eight. It strongly influences the physical properties of the final rubber article. Short crosslinks give the rubber better heat resistance. Crosslinks with higher number of sulfur atoms give the rubber good dynamic properties but with lesser heat resistance.

Vulcanization (and this applies to many of the materials in the previous chapter) is usually performed with sulfur, and that is why so many elastomer structures have a double bond. Other vulcanizing agents are possible, for example, peroxides (used with ethylene-propylene rubbers, Section 5.2.5), urethane crosslinkers, metallic oxides, and room temperature vulcanizing silicones. Vulcanizing formulations include accelerators, activators such as zinc oxide and stearic acid, and other materials that catalyze or inhibit the curing process. They are beyond the scope of this book.

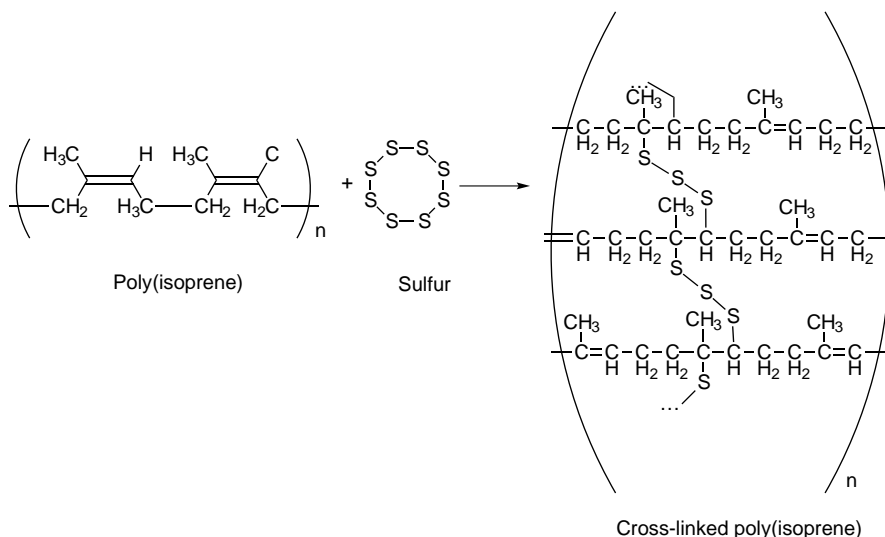
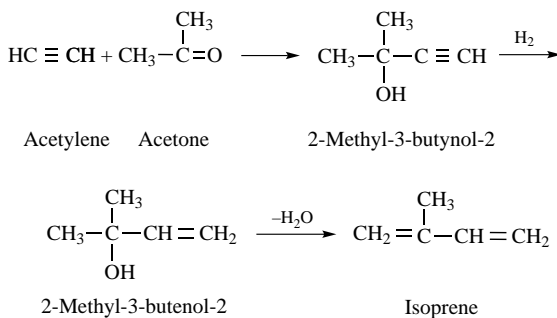


FIGURE 8.3 Vulcanization of rubber. (Source: <http://en.wikipedia.org/wiki/Vulcanization>.)

8.2.3 Production of Petrochemical Isoprene

The 2009 global market for isoprene was estimated at about 800,000 metric tons per year. It has three possible sources starting with the C₅ fraction, all mentioned in Section 8.1. The first is isolation from the C₅ fraction from steam cracking, the second is dehydrogenation of isopentenenes, and the third is dehydrogenation of isopentane.

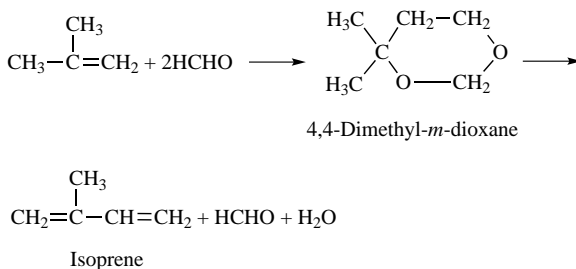
There are several synthetic routes to isoprene. In an Italian process devised by Snamprogetti, acetylene reacts with acetone to yield 2-methyl-3-butyne-2-ol. Hydrogenation gives 2-methyl-3-butenol, which on dehydration provides isoprene.



The condensation of acetylene and acetone is carried out in liquid ammonia at low temperatures with potassium hydroxide as the catalyst. The hydrogenation must be

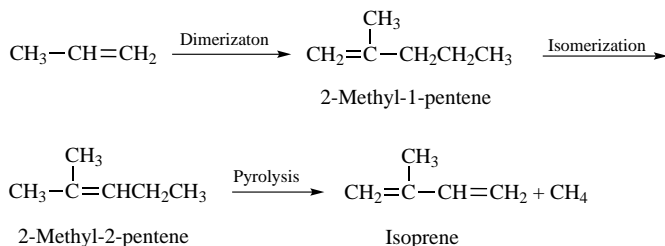
carried out selectively so that only the triple bond is attacked and converted to a double bond. This is reminiscent of the hydrogenation of 1,4-butynediol to 1,4-butenediol (Section 12.3.1). The dehydration goes well at 250–300°C with alumina. Snamprogetti operated a 30,000 metric ton/year plant until 1982.

A second process, devised by the Institut Français du Pétrole and said to be used in the CIS, involves the reaction of isobutene with formaldehyde, via the Prins reaction, to give 4,4-dimethyl-1,3-dioxane, which can be cracked to isoprene.

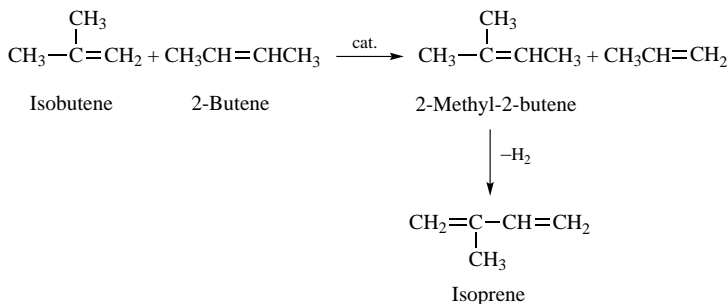


The Prins reaction is catalyzed by strong acid or acid ion exchange resin. Raffinate I (Section 7.1) may be used instead of pure isobutene. The second step of the reaction requires a high temperature with a phosphoric acid/charcoal or calcium phosphate catalyst with water.

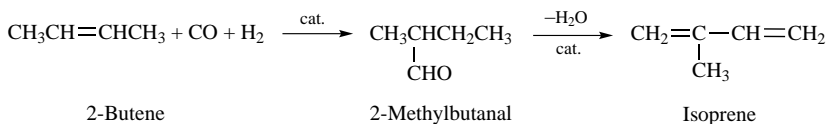
Another synthetic process, used only briefly by Goodyear because it proved uneconomical, involves the dimerization of propylene to 2-methyl-1-pentene (Section 6.3) followed by demethanation. The reaction goes in 90% yield at about 300°C and elevated pressures with a tri-*n*-propylaluminum catalyst. The dimer is isomerized at about 100°C with a silica–alumina catalyst to the more stable 2-methyl-2-pentene, which in turn is demethanated to isoprene and methane at 660°C in the presence of superheated steam and catalytic amounts of hydrogen bromide.



An attractive process for isoprene formation, which has never been commercialized, involves a metathesis reaction between isobutene and 2-butene to yield propylene and 2-methyl-2-butene which, as indicated above, can be dehydrogenated to isoprene.

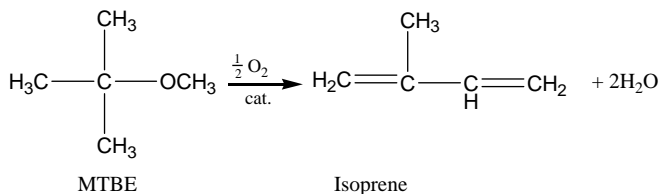


A clever synthesis of isoprene, also not commercialized, involves the hydroformylation of 2-butene with a rhodium catalyst such as rhodium (cyclooctadiene) acetylacetonate with triphenylphosphine at 115°C and 8 bar. A branched aldehyde, 2-methylbutanal, results.



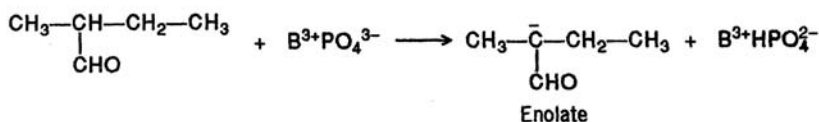
With a cobalt catalyst, a linear compound would form because cobalt facilitates migration of the double bond to the terminal position, a property important in the hydroformylation step of the Shell SHOP process (Section 5.3.4). The 2-methylbutanal is dehydrated with crystalline boron phosphate catalyst. Conversion to isoprene is 80%, with 85% selectivity. A proposed mechanism for the dehydration is shown in Figure 8.4. It is unusual for aldehyde groups to participate in this type of dehydration reaction.

Yet another route to isoprene that has been under investigation is Sumitomo's air oxidation of MTBE using molybdenum, tungsten, or vanadium oxide catalysts:

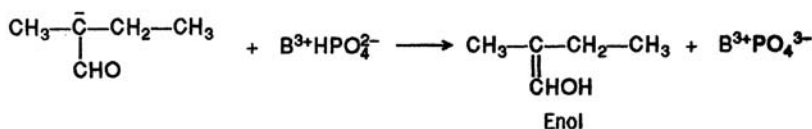


Genecor, in collaboration with The Goodyear Tire and Rubber Company, is developing a biotechnological route to so-called bio-isoprene. Genecor has engineered *E. coli* bacteria capable of converting sugars to isoprene. Commercialization of this technology is targeted for 2012.

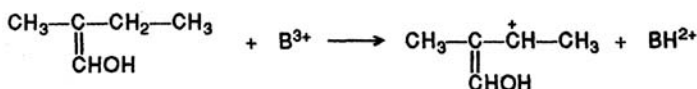
(a) Enolization:



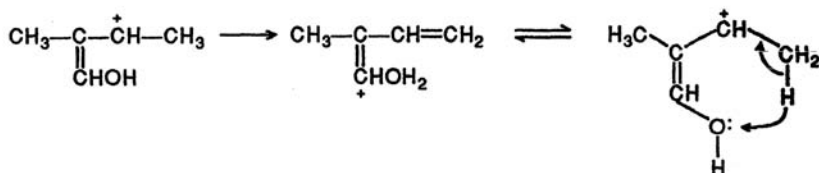
(b)



(c) Hydride abstraction:



(d) Hydride shift:



(e) Displacement of water by hydride:

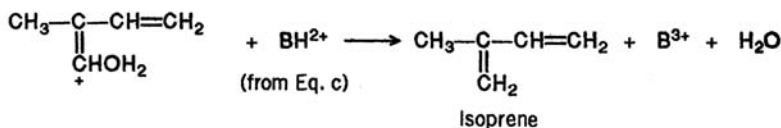


FIGURE 8.4 Proposed method for the production of isoprene by dehydration of 2-methylbutanal.

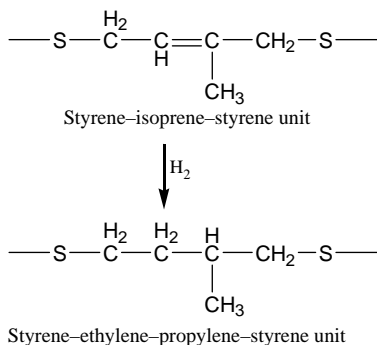
8.2.4 Applications of Isoprene

The major use for isoprene is its stereospecific polymerization to *cis*-1,4-polyisoprene, a polymer closely related to natural rubber.³ Its preparation was not possible prior to the advent of Ziegler–Natta catalysis. The catalyst may comprise a titanium tetrachloride/trialkylaluminum combination or an alkyllithium. Modern radial ply tires require increased amounts of natural rubber because it has greater resilience and lower hysteresis losses, that is, less heat buildup than styrene–butadiene rubber. The demand can be satisfied with synthetic *cis*-1,4-polyisoprene, provided

that it is competitive in price with natural rubber. The increasing consumption of natural rubber was illustrated in Figure 7.5.

The second important use for isoprene is in styrene–isoprene–styrene (S-I-S) block copolymers similar to S-B-S copolymers (Section 7.1.2). These thermoplastic elastomers contain about 85% isoprene and 15% styrene and are used in applications where elasticity combined with easy processing is desired. These include bitumen/asphalt modification, adhesives, sealants, and coatings, polymer modification, and polymers for footwear soles and heels. S-I-S block copolymers are made commercially in a semicontinuous process (the polymerizations are carried out batchwise while the polymer and solvent recovery stages are run continuously). Batch polymerization makes it easier for the producer to control the extent of polymerization and provides flexibility for production of various product grades. The heart of the process is the block polymerization reaction that can be divided into three separate stages: styrene polymerization, diene polymerization, and finally coupling of the “living” polymer chains (Section 17.3.7). In the first polymerization stage, styrene is polymerized in cyclohexane with butyllithium as the initiator. After about 1 hour, the resulting polystyryllithium living polymer solution is transferred rapidly into a separate reactor containing isoprene in cyclohexane. Isoprene polymerization is initiated via the polystyryllithium and is completed in about 2 hours. At this stage a two-block polystyrene–polyisoprenyllithium species is present. Finally, the S-I-S block copolymer can be made in one of two different ways. In one way the two-block copolymer is coupled with a coupling agent such as dibromoethane. In the other, the additional styrene is added to the living two-block chain to give a linear three-block polystyrene–polyisoprene–polystyrene copolymer.

An extension of S-I-S technology is the hydrogenation of the polymers to produce styrene–ethylene–propylene–styrene (S-E-P-S):



These partially hydrogenated polymers were initially developed by Shell using a high pressure hydrogenation step, but they sold the business in 2001. Kuraray is reportedly working on a lower cost process employing low pressure hydrogenation technology. The hydrogenated derivatives have the advantage of increased weather and temperature resistance.

Another use for isoprene is in the manufacture of butyl rubber, a copolymer of isobutene and 3–5% isoprene (Section 7.2.2), which shows very low gas permeability and is used to line tires. This is an example of the different reactivities of isoprene's two double bonds. The more reactive participates in chain formation, whereas the less reactive double bond is pendant and makes possible further reactions including curing or vulcanization with sulfur.

A small volume isoprene derivative is *trans*-1,4-polyisoprene. The *trans* double bond makes the molecule crystalline, removing all the elastomeric properties of the *cis* isomer. The product resembles two natural materials, balata and gutta percha, and is useful for golf ball covers. This use has declined because of the superior properties of ionomers such as "Surlyn" (Section 5.2.3). Gutta percha is still used by dentists for temporary fillings for teeth, particularly in "root canal" work. Balata and gutta percha are both polyisoprenes and are believed to be stereoisomers.

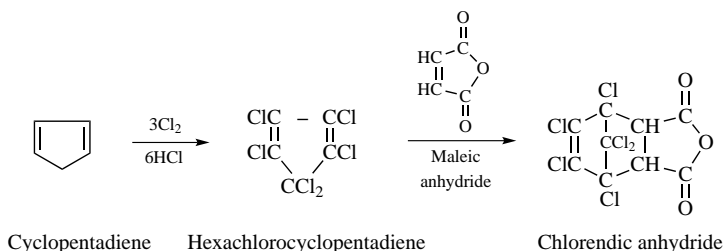
8.3 CYCLOPENTADIENE AND DICYCLOPENTADIENE

Cyclopentadiene is typically the largest component in the C₅ stream from standard severity steam cracking of naphtha and accounts for 15–25% of the total C₅ fraction. It also occurs in distillate from coke ovens. Like butadiene, it is not formed in catalytic cracking. The U.S. demand in 2009 was estimated at about 170,000 metric tons.

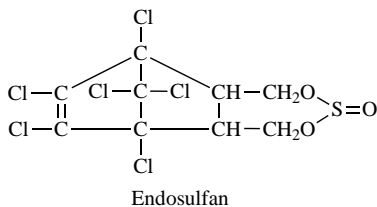
Owing to the difficulty of separating cyclopentadiene from the other close boiling C₅ olefins in the C₅ stream, it is usually recovered as its dimer, dicyclopentadiene (Section 8.1).

The main use for cyclopentadiene is in the formulation of inexpensive low molecular weight (under 2000) oligomers, which fall into the category of hydrocarbon resins. There are two types, linear aliphatic and cycloaliphatic. The former are made from unsaturated C₅ cuts containing primarily piperylene (1,3-pentadiene) and pentenes. The cycloaliphatics contain these and cyclopentadiene. The resins are used in thermoplastic and contact adhesives and in printing inks. In rubber formulations, they increase hardness and flex life.

The liquid phase chlorination of cyclopentadiene provides hexachlorocyclopentadiene, which undergoes a Diels–Alder reaction with maleic anhydride to form so-called chlorendic anhydride, used as a flame retardant in unsaturated polyester resins (Section 11.1.3).



Hexachlorocyclopentadiene undergoes a similar Diels–Alder reaction with 1,4-dihydroxy-2-butene (Section 12.3.1) to give a diol adduct, which reacts with thionyl chloride to give the insecticide, endosulfan.

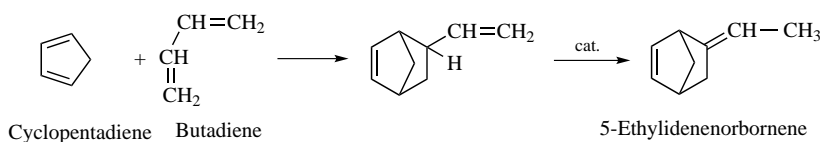


Like most organochlorine compounds, endosulfan is suspect because its persistence leads to its accumulation in the food chain and subsequently in body fat. As this book goes to press, the Stockholm Convention on Persistent Organic Pollutants has agreed to a global moratorium on its use although 14 crops were exempted for a five-year phase-out period.

An emerging application for cyclopentadiene is as starting material for monomers for use in cyclic olefin copolymers (COCs). COCs are amorphous transparent polymers made via copolymerization of ethylene with cyclic olefin monomers such as norbornene and tetracyclododecene. Norbornene is made by the Diels–Alder reaction of ethylene and cyclopentadiene and tetracyclododecene is made by the Diels–Alder reaction of cyclopentadiene and norbornene. It is believed that COCs, because of their good optical and physical properties, may present a lower cost alternative to polycarbonate for CD-ROMs, although commercialization has been slow.

The main use for dicyclopentadiene is in unsaturated polyester resins (Section 11.1.3), where it terminates the maleate ester chains. In addition, dissociated cyclopentadiene enters Diels–Alder reactions with the double bonds in the unreacted maleate esters. The result is a low viscosity resin with high strength. An added benefit is that less styrene reactive diluent is required, making this a more environmentally friendly system. The product is said to be more brittle but to have a smoother surface.

Because dicyclopentadiene has two double bonds of varying reactivity, it can be used as a monomer in ethylene–propylene diene monomer elastomers (Section 5.2.5). In this application it competes with *trans*-1,4-hexadiene (Section 7.1.6.6) and 5-ethylidenenorbornene. The latter results from a Diels–Alder condensation of cyclopentadiene and butadiene. The adduct is isomerized with an alkaline earth metal catalyst to 5-ethylidenenorbornene.



In all these compounds, the active double bond enters into the copolymerization leaving the less active double bond pendant for crosslinking or vulcanization with sulfur-containing compound as mentioned above.

In an interesting application, dicyclopentadiene is a monomer for the production of a thermoset polymer useful in reaction injection molding (RIM).⁴ In conventional injection molding, the size of moldings made from viscous polymers like polyethylene is limited by the amount of pressure available to push the molding compound into the mold. In RIM, low molecular weight components react in a mold almost instantaneously. The advantage is that large moldings can be made. Dicyclopentadiene undergoes ring opening metathesis polymerization (Section 4.14) in the mold in the presence of a catalyst, comprising tungsten hexachloride in *p*-*tert*-butylphenol, to give a crosslinked polymer.

Dicyclopentadiene can be oxidized to maleic anhydride but this reaction has never been commercialized.

8.4 PENTENE-1 AND PIPERYLENE

Pentene-1, while present in C₅ steam cracker streams, is rarely isolated. However, a much larger source of pentene-1 is available in Sasol's Fischer-Tropsch "Synthol" stream (Section 14.2). The uniqueness of olefins in the Synthol stream is that a large percentage are linear α -olefins with both odd and even numbers of carbon atoms. Ethylene oligomerization, the conventional route to α -olefins, gives only even carbon numbered compounds (Section 5.3.2). Pentene-1 has potential application as a comonomer in linear low density polyethylene, but because of the historical lack of supply and even now only a single supplier, adoption of pentene-1 as a comonomer has been very slow. Meanwhile, Sasol is developing copolymers of pentene-1 and propylene. Adding pentene-1 in 1–5% amounts gives copolymers with higher clarity improved gloss and higher metal strength. They are easier to process than conventional polypropylene resins. Piberylene (1,3-pentadiene) is used almost entirely in premium aliphatic hydrocarbon resins.

ENDNOTES

1. Separation technologies for C₅s are discussed in Nexant ChemSystems Process Evaluation/Research Planning (PERP) report 98/99S4, *Options for Refinery C₅s* (September 1999).
2. R. Teresi, *Lost Discoveries*, Simon & Schuster, New York, 2002, pp. 337–340; D. Hostler et al., *Science*, 18 June 1999, pp. 1988–1989.
3. Nexant ChemSystems Process Evaluation/Research Planning (PERP) report 98/99S2, *Isoprene* (September 1999).
4. Nexant ChemSystems Process Evaluation/Research Planning (PERP) report 97/98S7, *Dicyclopentadiene and Derivatives* (August 1998).

CHAPTER 9

Chemicals from Benzene

In 2008, about 5.6 million metric tons of benzene was used in the United States as a chemical feedstock as compared to 14.78 million metric tons of propylene (Section 1.5). The corresponding figures for Western Europe were 7.62 and 14.76 million metric tons. This makes benzene the third most important basic chemical; but it has declined in relative importance. Until the mid-1970s, it was in greater demand than propylene, but the astonishing growth of polypropylene has left it trailing behind.

Benzene has four sources. Traditionally, it came from coke oven distillate, itself dependent on demand for coke for steelmaking. Second, it comes from steam cracking of liquid feedstocks, which is driven by ethylene demand; and third, it comes from the catalytic reforming of naphtha, which is governed by the gasoline market. Finally, it comes from hydrodealkylation or disproportionation of the toluene that is produced in far greater quantities from catalytic reforming than the market demands.

In the United States, most benzene (38%) comes from the catalytic reforming of naphtha (Section 4.8) which yields a mixture of benzene, toluene, and the xylenes (BTX). The traditional source of benzene was as a volatile by-product of the conversion of coal to coke. Benzene from coke oven distillate (coal tar) is available only to the extent that coke is required by the steel industry, and this has not expanded to accommodate the expanding benzene market. Furthermore, such benzene contains sulfur-based impurities such as thiophene that are difficult to remove, and these render it unacceptable for many purposes. In 1949 all U.S. benzene was produced from coal tar; by 1959 the proportion had dropped to 50%. In 1972 it was down to only 6.4%, and in the early 2000s it was about 1%.

That is not the whole story, however. In Europe and Japan, pyrolysis gasoline (Section 4.5.1) is the major source of benzene and toluene. It results from the steam cracking of hydrocarbons, particularly naphtha and gas oil. Xylenes also occur in pyrolysis gasoline but are not easily isolated because of a high concentration of ethylbenzene. In the United States only 33% of benzene comes from this source, but in Western Europe it is 60%. Figure 9.1 shows the sources of benzene worldwide and Figure 9.2 shows the global primary production of aromatics, that is, neglecting the

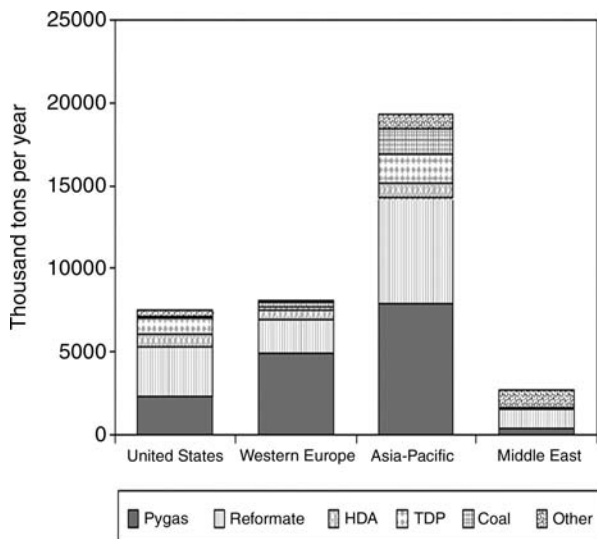
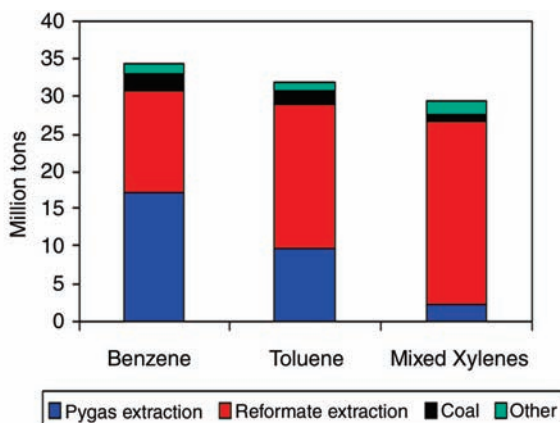


FIGURE 9.1 Regional benzene production 2009. Pygas = pyrolysis gasoline; HDA = hydrodealkylation; TDP = toluene disproportionation. (Source: Nexant Inc.)

contribution of hydrodealkylation of toluene to benzene and related processes. Somewhat more benzene comes from coke oven distillate in Europe than in the United States.

Catalytic reforming typically leads to a benzene, toluene, xylenes (BTX) mixture containing about 50–55% toluene, 30–35% xylenes, but only about 10–15% benzene, the end product most in demand for chemical production (see Table 4.10). Toluene and the xylenes, on the other hand, have been favored for raising the octane number of



**Note that much of the toluene produced in the reformer is not extracted and stays in the reformate for gasoline blending. Other primary sources include production from LPG.*

FIGURE 9.2 Primary production of aromatics (2009 estimates). (Source: Nexant Inc.)

unleaded gasoline and they are less toxic than benzene. Since there have always been large surpluses of chemical toluene, a process was devised to convert toluene to benzene by hydrodealkylation (Section 10.1). In 2001 this accounted for about 7% of U.S. and 11% of West European toluene consumption, down from 24% and 28%, respectively, in the early 1990s. By 2009, 82% of toluene was converted to benzene. The amount of toluene hydrodealkylated fluctuates partly because it is a function of the price differential between benzene and toluene. Toluene must be at least 15% cheaper to warrant hydrodealkylation. Hydrodealkylation also assumed less importance in the United States by the early 2000s because it was largely replaced by toluene disproportionation (Section 10.1). By 2009, hydrodealkylation accounted for 7% of U.S. benzene and disproportionation 15%. The corresponding figures in Western Europe were 6% and about 1%. This shift was motivated by the fact that disproportionation provides *p*-xylene, the demand for which has burgeoned in the Far East since the late 1980s as feedstock for terephthalic acid for poly(ethylene terephthalate).

The U.S. Clean Air Act, which came into effect in 1995, changed the aromatics supply picture. It stipulates that benzene in gasoline must be decreased to 1% and the remaining aromatics content must be no greater than 25%. In 1990, gasoline contained as much as 3% benzene and 36% total aromatics. Thus catalytic reforming (Section 4.8) must be carried out as usual for benzene, toluene, and xylenes (BTX) for the chemical industry, but for gasoline, naphtha, stripped of the C₅ and C₆ fraction, must be lightly reformed to produce as little benzene as possible.

Catalytic reforming works best with C₇ and C₈ molecules but less well with C₆ alkanes, which tend to form cracked products, thus reducing the yield of benzene. Also higher temperatures are required to reform C₆ alkanes. Thus, by using lower temperatures, the C₇ and C₈ molecules reform preferentially. If the naphtha is stripped before reforming, most of the C₆ alkanes are removed so that benzene cannot form. Even so, benzene results in the reforming process from hydrodealkylation of the toluene and xylenes.

In the early 1990s, Chevron instituted a catalytic reforming process called Aromax, based on a metal-doped zeolite catalyst, which reforms the C₆ fraction more effectively to give a higher yield of benzene.¹

The upshot of all this is that the United States is chronically short of benzene, and Western Europe needs to import to make up the shortfall from pyrolysis gasoline. Both regions need to import benzene, which is not a problem in that benzene is a liquid and easy to handle (Table 9.1). The required material is supplied primarily by

TABLE 9.1 World Benzene Trade (million metric tons)^a

Region	1997	2002	2009
North America	(235)	(1213)	(1144)
Western Europe	(417)	(194)	(553)
Asia-Pacific	(95)	127	956
Middle East	83	387	194
South America	254	186	125

^a Figures in parentheses represent net imports.

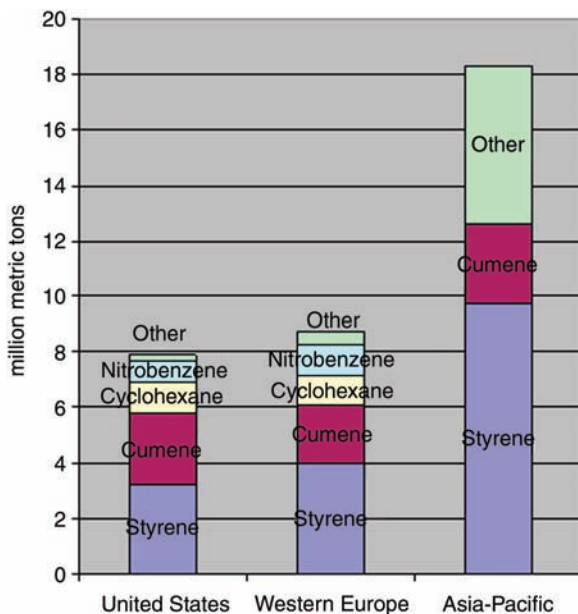


FIGURE 9.3 Global benzene demand (2009).

Asia-Pacific, which cracks mainly liquid feedstocks. It is significant that the region has moved from a deficit in 1997 to being the world's supplier in 2009.

The major uses for benzene are shown in Figure 9.3. In addition to these we shall discuss a number of small volume chemicals from benzene. The biggest use for benzene is its reaction with ethylene to give ethylbenzene for dehydrogenation to styrene and for peroxidation to ethylbenzene hydroperoxide for propylene oxide and styrene (Section 5.8). These processes have already been described. Next is its reaction with propylene to give cumene for conversion to phenol and acetone (Section 6.6). In 2009 ethylbenzene and cumene accounted for just over 70% of global benzene consumption.

9.1 PHENOL

Phenol is yet another chemical for which a variety of processes are available. The cumene hydroperoxide process, by far the dominant process, was described in Section 6.6, but there are various obsolete routes. The earliest process was the sulfonation of benzene to benzenesulfonic acid followed by fusion of the sodium salt of the acid with alkali (Fig. 9.4a). During the Boer War (1899–1902) the British used picric acid (trinitrophenol), an uncertain and unreliable explosive, in their shells. The phenol in coal tar did not provide enough picric acid for the war effort, and the benzenesulfonate process thus became the first tonnage organic chemical process to be operated. Large amounts of by-product Na_2SO_3 and NaHSO_3 made this process cumbersome. To be economical, a benzenesulfonate plant requires cheap sulfuric acid

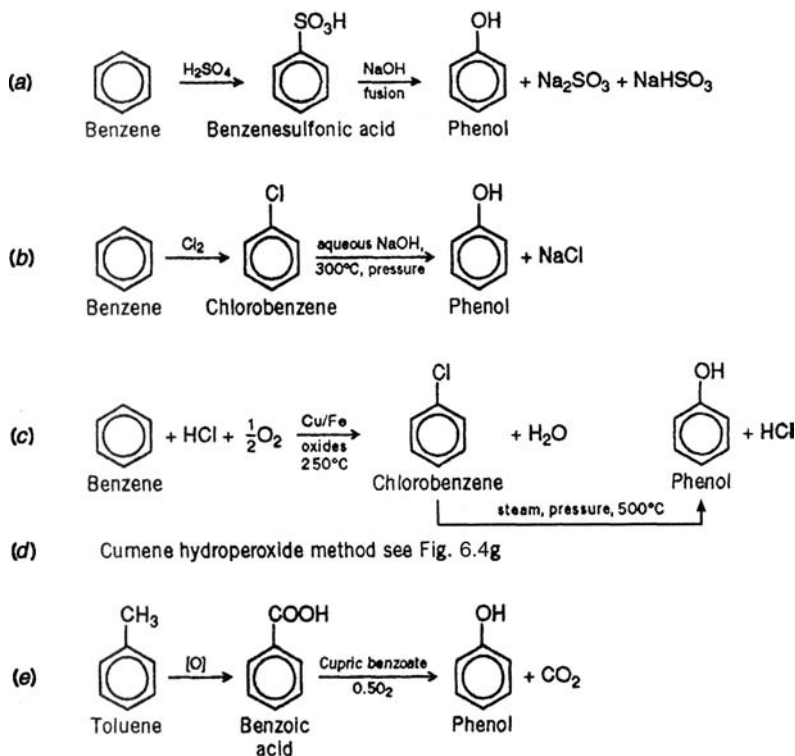


FIGURE 9.4 Processes for phenol manufacture.

and caustic soda, and a nearby paper mill to use the sodium sulfite by-product for pulping. Labor costs are high but capital costs are low. No synthetic phenol is made in this way now in either the United States or Western Europe.

The second route appeared in 1924 (Fig. 9.4b) and involved the direct chlorination of benzene to chlorobenzene, which was then hydrolyzed to the sodium salt of phenol by means of sodium carbonate or sodium hydroxide. The chlorobenzene process is expensive because of chlorine and alkali usage and must be operated on a very large scale to be economical. Dow–Midland closed their massive 100,000 tons per year plant in 1975 and Bayer followed suit in 1977. Thus no U.S. or European synthetic phenol is made in this way.

In a later process, the Raschig–Hooker regenerative process (Fig. 9.4c), chlorobenzene was prepared from hydrogen chloride, air, and benzene [a reaction comparable to the oxychlorination of ethylene (Section 5.4)] at 250°C with a $\text{CuCl}_2/\text{FeCl}_3$ catalyst supported on alumina. Hydrolysis by steam in the vapor phase with a $\text{Ca}_3\text{PO}_4/\text{SiO}_2$ catalyst at 450°C yields phenol and HCl for recycle. The oxychlorination is run to a conversion of only 10–15% to diminish dichlorobenzene formation, which takes place to the extent of 6–10%. In the hydrolysis of the chlorobenzene, diphenyl ether and *o*- and *p*-hydroxydiphenyl ethers are formed as by-products. The dichlorobenzenes are recycled to the chlorination reaction, their presence preventing the

formation of additional more highly chlorinated products. The Raschig–Hooker process requires highly corrosion-resistant equipment because of the presence of HCl at high temperatures. It is not as wasteful of chlorine and alkali as the chlorobenzene route, but conversions per pass are low, and therefore capital costs are high. Also the high temperatures and acid conditions cause corrosion problems, and the high pressures increase operating costs. The process has been obsolete since 1971.

Another reaction was motivated by surplus toluene (Fig. 9.4e) which is first oxidized in the liquid phase to benzoic acid. Molten benzoic acid then reacts with air and steam in the presence of cupric benzoate promoted with magnesium benzoate as catalyst. The volatile phenol is removed by distillation. This process, which gives a selectivity approaching 90%, has the advantage of starting with a lower cost raw material. However, the process was only a limited success, in part because the economics of the cumene process benefited from the acetone coproduct credit. The economics of toluene oxidation depend to a degree on whether toluene provides greater value in this reaction or in hydrodealkylation (Section 10.1). In the early 2000s, about 144,000 metric tons of phenol was manufactured by this route in the United States by Noveon, Inc. (originally Kalama) and by DSM in Western Europe. Nippon Phenol has 120,000 metric tons/year capacity in Japan. The process is economically feasible because valuable benzaldehyde and benzoic acid by-products are formed. In this sense, it is a two-for-one process like the cumene hydroperoxide process. It demonstrates, however, the tyranny of two-for-one reactions, namely, that for widespread use the two products must be produced in the ratio that the market demands. It is unlikely that this process will ever grow much beyond its current level as benzaldehyde and benzoic acid demand is limited. U.S. benzoic acid production in 2003 was only 64,000 metric tons. Plants are said to operate in the United States, the Netherlands, and Japan.

Although the mechanism for the conversion of benzoic acid to phenol is uncertain, it may proceed through phenyl benzoate, as shown in Figure 9.5. The phenyl benzoate decomposes to phenol and benzoic acid, and the cuprous benzoate is reoxidized to cupric benzoate. An alternative mechanism postulates the formation of salicylic acid or *p*-hydroxybenzoic acid, either of which may decompose to phenol and carbon dioxide.

The cumene process (Section 6.6) thus has much in its favor. No expensive chlorine, sodium hydroxide, or sulfuric acid is wasted; conditions are mild; and utility costs are low. Its sole drawback is that a demand must exist for both chemicals in the ratio in which they are produced. Market disruptions during the mid-1980s motivated research for a new process that produces phenol only. Thus a plant was built in Australia in which a cyclohexanol/cyclohexanone mixture (Section 9.2.1) was dehydrogenated to phenol, but it was soon closed as uneconomical. A Japanese process (Section 6.10) operates with cumene made from benzene and isopropanol rather than propylene. The isopropanol is made by hydrogenation of the surplus acetone produced in the process. In a related process, Mitsui Chemical is believed to dehydrate isopropanol back to propylene for recycle to the front-end of the cumene process. Mitsui uses this process when acetone demand is slack.

The direct air oxidation of benzene to phenol is a research goal.² One route involves the reaction of benzene with acetic acid in the presence of palladium and oxygen to

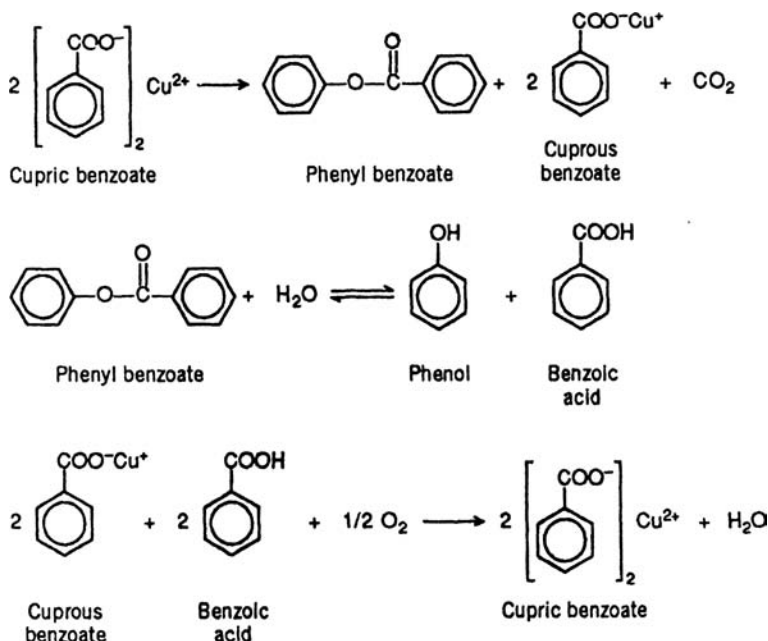
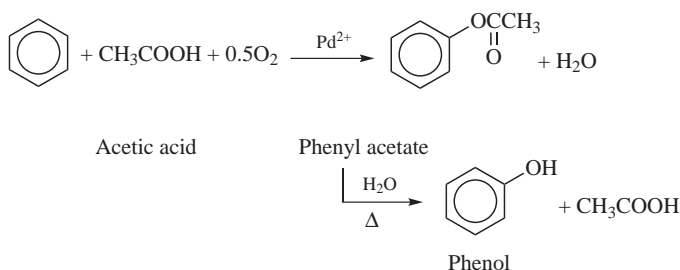


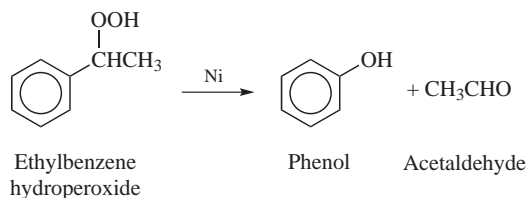
FIGURE 9.5 Conversion of benzoic acid to phenol.

give phenyl acetate. This reaction is analogous to the formation of acetaldehyde (Section 5.5) by the Wacker reaction or vinyl acetate (Section 5.6) by a related reaction.



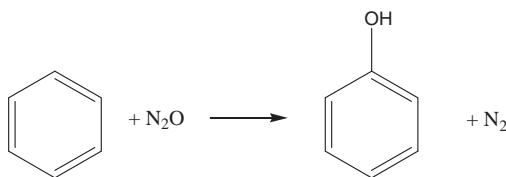
As in the Wacker reaction, the palladium is rendered catalytic by the incorporation of an oxidant. As in the vinyl acetate process, the reaction may be carried out in the vapor phase over a supported palladium metal catalyst. The phenyl acetate may then be hydrolyzed to phenol and acetic acid, which is recycled.

Ethylbenzene hydroperoxide (Section 6.8) may be decomposed with a nickel catalyst to phenol and acetaldehyde in very high yield. However, this too is a coproduct process and the demand for acetaldehyde had decreased by the mid-1980s (Section 5.5).

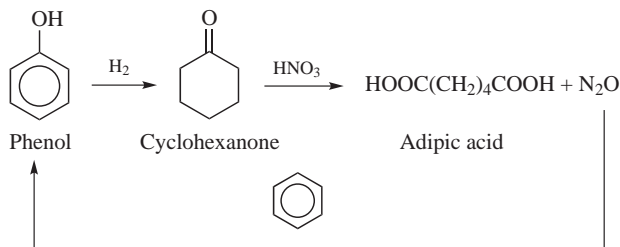


Asahi Chemical has developed a process for the production of phenol from benzene via selective hydrogenation to cyclohexene. About 20% of the cyclohexene is unavoidably further hydrogenated to cyclohexane. Cyclohexene is separated from the cyclohexane and unconverted benzene by a series of extractive distillations. The purified cyclohexene is either oxidized to a mixture of cyclohexanone, cyclohexenone, and cyclohexanol or hydrated to cyclohexanol. These oxygenated compounds are finally dehydrogenated to phenol. The cyclohexane could be dehydrogenated to benzene for recycle.

In the mid-1990s, Solutia (formerly Monsanto) developed a direct route to phenol in collaboration with the Boreskov Institute of Catalysis in Russia.³ It was based on the discovery by a Japanese professor in 1983 that certain metal impregnated zeolites could catalyze the oxidation of benzene to phenol with nitrous oxide as oxidant. Selectivity to phenol is over 95%.⁴



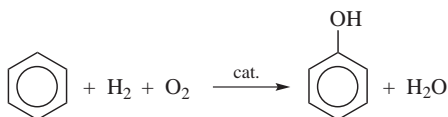
One of the drawbacks to this approach is that it requires a low cost source of nitrous oxide. Solutia had an answer to this. Nitrous oxide is an unavoidable by-product of modern adipic acid production (Section 9.2.1), by a process already operated by Solutia. Nitrous oxide is a greenhouse gas and must be safely disposed of. Thus the Solutia phenol process takes a process debit and converts it into a process credit.⁵ It also offered the opportunity to couple phenol and adipic acid production:



Solutia had announced their intent to commercialize this process, but because of overbuilding of phenol plants, their plans were put on hold in 2001. Solutia has sold its nylon business, and the project does not seem to have been resumed. A problem is that a relatively small phenol plant requires a world-scale adipic acid plant for its nitrous oxide supply. Only two other U.S. companies have by-product nitrous oxide from adipic acid production.

If required, nitrous oxide can be produced by the catalytic oxidation of ammonia. This chemistry is used in Japan for making small quantities of very high purity nitrous oxide for medical application. It would be a significant development if this approach gave nitrous oxide at low enough cost to make the Solutia process competitive with the conventional cumene-based route.

The Korea Research Institute of Chemical Technology has developed a one-step route to phenol by the passage of hydrogen, oxygen, and nitrogen into a 50:50 solution of benzene and acetic acid at 50°C containing a slurry of two different zeolite catalysts.



Ninety-seven percent selectivity is claimed with a zeolite mixture also containing palladium and ethylanthraquinone. The latter presumably promotes formation in situ of hydrogen peroxide. The snag is that the catalyst has low productivity before regeneration is required.

Japanese researchers at the Institute for Materials and Chemical Processes, National Institute of Advanced Science and Technology have discovered a one-step benzene to phenol process. In the Japanese process, benzene, oxygen, and hydrogen are passed over a catalyst composed of palladium supported on alpha-alumina at 250°C. Phenol was produced in over 90% selectivity but per pass conversions were less than 3%.

As the above examples show, the “holy grail” of phenol production technology – direct benzene hydroxylation with either oxygen or hydrogen peroxide – remains distant. While some progress has been reported, catalysts capable of achieving both high selectivity, activity, and run length have eluded researchers.

9.1.1 Phenolic Resins

The major applications for phenol are shown in Figure 9.6. The biggest use in the past was the manufacture of phenol–formaldehyde resins (Section 17.4.1) but it has now been overtaken by bisphenol A. Globally, in 2009, 3.3 million metric tons of phenol went into bisphenol A and 2.0 million into phenolics.

Phenolic resin production in the United States in 2009 was 1.92 million metric tons. Phenolic resins have good chemical, heat, and water resistance, good dielectric properties, and high surface hardness and dimensional stability. They are

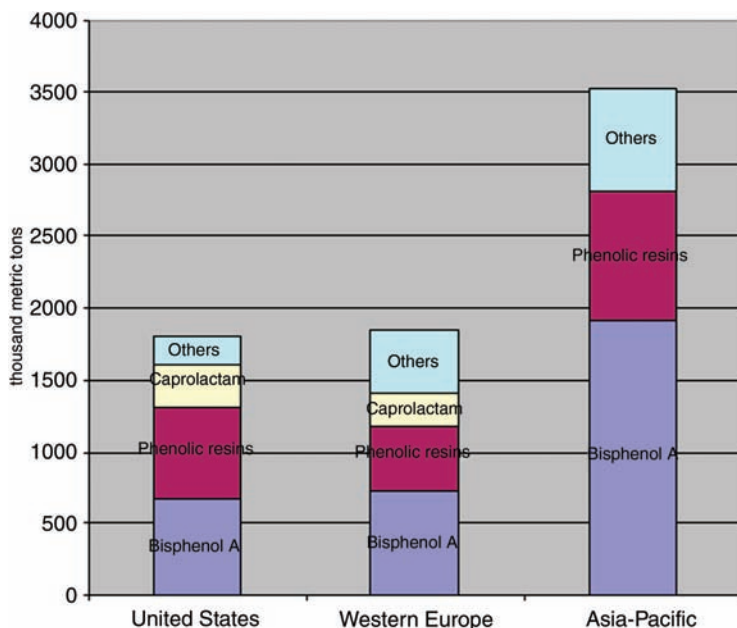


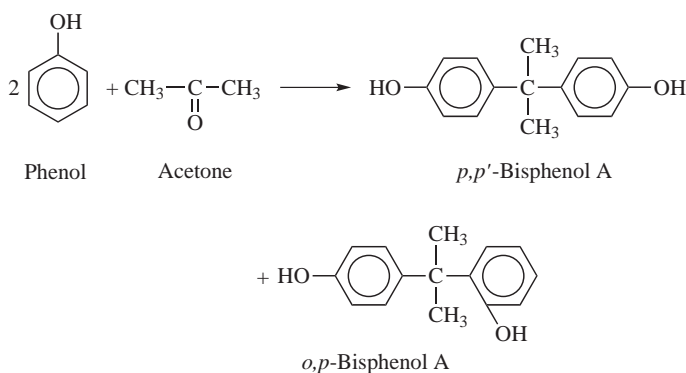
FIGURE 9.6 Phenol end-use pattern (2009). “Others” include caprolactam for Asia-Pacific and (everywhere) adipic acid and aniline. Western European adipic acid consumption was 57,000 metric tons and Asia-Pacific online was 72,000 metric tons.

cheap and can be formulated to meet the needs of the electrical, automotive, appliance, and adhesives industries. Adhesives comprise the largest market for phenolic resins, with bonding of plywood, particle board, and hardboard the largest single application. Phenolic resins are also used in the fabrication of laminates such as “Formica” in which a phenolic bound composite, with an unattractive brown color, is faced or coated with a layer of a high-quality, colorless, non yellowing melamine–formaldehyde resin. Under the layer is placed the pattern – often an actual photograph of wood grain or, in cheaper formulations, a printed picture of wood grain. Phenolic resins are frequently compounded with other adhesives to provide water resistance and tack or stickiness.

Phenolic moldings inevitably have a poor color, and they can be produced only in dark colors. They are used for the characteristic electrical plugs and were formerly used for telephones. Other applications include insulation, abrasives, and foundry and shell moldings. They are used in brake linings, clutch facings, and other friction parts where a high temperature-resistant binder is required. Phenolics are also crosslinking agents for epoxy resins in the formulation of structural adhesives and resistant coatings, particularly for can linings. Although usage is large, growth has been inhibited, as it has been for all thermoset resins, because of the difficulty of fabrication and the low molding speeds. The water resistance of the resins is a positive point but the poor color a negative one.

9.1.2 Bisphenol A

Phenol condenses with acetone to give bisphenol A, which in turn reacts with epichlorohydrin to give epoxy resins (Section 9.1.2.1) and with phosgene to give polycarbonates (Section 9.1.2.2). In the early 2000s, the production of bisphenol A became the largest consumer of phenol. For epoxy resins a mixture of the *o*- and *p*-isomers is acceptable, but the other polymers require the *p,p'*-isomer.



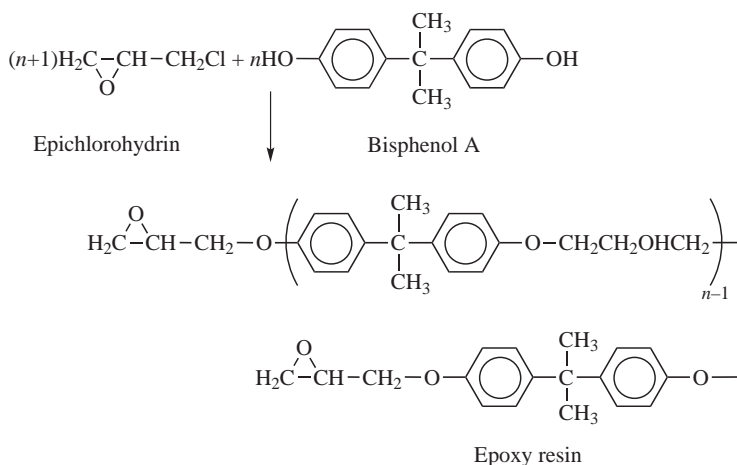
Polycarbonate grade bisphenol A is 99.5% pure whereas the epoxy grade is 95% pure and is a mixture of the two isomers. The condensation of acetone and bisphenol A was traditionally catalyzed with hydrogen chloride at about 50°C. The substitution of a solid catalyst, such as a sulfonated cation exchange resin, for the corrosive hydrogen chloride provides a more ecologically acceptable reaction because disposal of the spent hydrogen chloride is fraught with problems. The ion exchange resin is used at 70–90°C. It leads to production cost savings of 15 cents per kilogram in a 90,000 metric ton per year plant. Materials of construction are cheaper, less maintenance is required, waste water production is minimal, and treatment facilities and product purification are simpler.

A variety of by-products are produced and these can be rearranged to bisphenol A at 75°C in the presence of a catalyst comprising a cation exchange resin partially esterified with a mercaptoalcohol.

The separation of the *o,p*-isomer from the *p,p*-isomer is accomplished by a combination of distillation and crystallization. In the United States in 2009, 73% of bisphenol A was required for production of polycarbonate resins and 21% for epoxy resins. In Western Europe, polycarbonates take 67% and epoxy resins 29%. Other uses include polysulfones, poly(ether imides), polyarylates, and specialty polyester resins as well as tetrabromobisphenol A fire retardants (see below).

9.1.2.1 Epoxy Resins

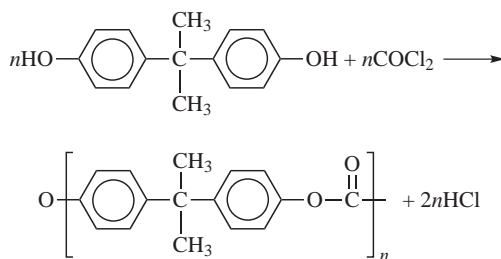
Epoxy resins (Section 17.4.3) are oligomers resulting from the condensation of bisphenol A and epichlorohydrin (Section 6.11.1).



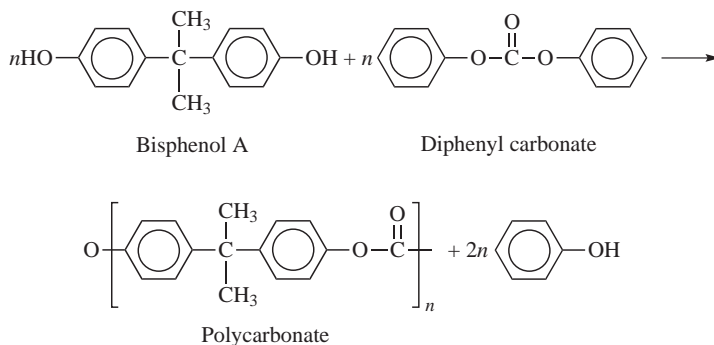
When crosslinked they provide hard, chemically resistant, and dimensionally stable polymers with superb electrical properties. Their largest use is for protective coatings for metal containers, appliances, and ships, as well as for general maintenance where resistance to severe corrosion is required. They are used in the computer industry for “potting” electrical components. The second largest use is in fiber-reinforced composites for circuit boards, aerospace components, and sporting equipment. Other uses include adhesives, sealants, patching and flooring compounds, and castings. U.S. production in 2008 was 264,000 metric tons.

9.1.2.2 Polycarbonate Resins

The conventional route to polycarbonate resins is via the condensation of bisphenol A and phosgene. They are thermoplastics with exceptional clarity, impact strength, and flame resistance, and they do not warp. The problem of reacting a high melting solid, the sodium salt of bisphenol A, with a gas, phosgene, has been solved by the use of phase-transfer catalysis (Section 18.10). The salt is made into a slurry in water, whereas the phosgene is dissolved in an organic phase such as dichloromethane containing a catalytic amount of a base such as pyridine. A 1995 General Electric patent⁶ suggests that they now prefer tetrabutylammonium hydroxide in 50% sodium hydroxide solution, which permits the use of a phosgene excess of only 2% compared with a 30% excess required in the older method, because of hydrolysis.⁷ The phosgene–pyridine complex is sufficiently lipophilic so that it migrates to the organic layer where the condensation takes place. The pyridine returns to the aqueous layer to repeat the operation. This was probably the first industrial use for phase transfer catalysis.



Phosgene is highly toxic; indeed it was used as a poison gas in World War I. In the early 1990s, General Electric built a polycarbonate plant in Japan that did not use phosgene, and other companies, such as Bayer and Asahi, have developed similar routes. It is believed that all the nonphosgene-based plants use the same basic reaction to produce polycarbonate. Diphenyl carbonate, prepared without phosgene, as indicated below, is reacted with bisphenol A in the absence of solvent to give an intermediate low molecular weight prepolymer and phenol, which is reused to make additional diphenyl carbonate. The prepolymer is further heated under high vacuum to build molecular weight. Regenerated diphenyl carbonate is recycled. This transesterification process, also called the melt process, has an advantage over the commonly used interfacial route in that the product is obtained in undiluted form and may be made directly into pellets. Disadvantages of the melt process are the high vacuums needed, and limitation on molecular weight imposed by the high melt viscosity.



While all producers of nonphosgene polycarbonate use the meltphase transesterification process described above, they use different technologies to make the diphenyl carbonate and diphenyl carbonate precursors. For instance, it is believed that GE Plastics uses the route shown in Figure 9.7, starting with the oxidative carbonylation of methanol to dimethyl carbonate (Section 12.5.2.5).⁸ An exchange reaction between phenol and dimethyl carbonate provides diphenyl carbonate.

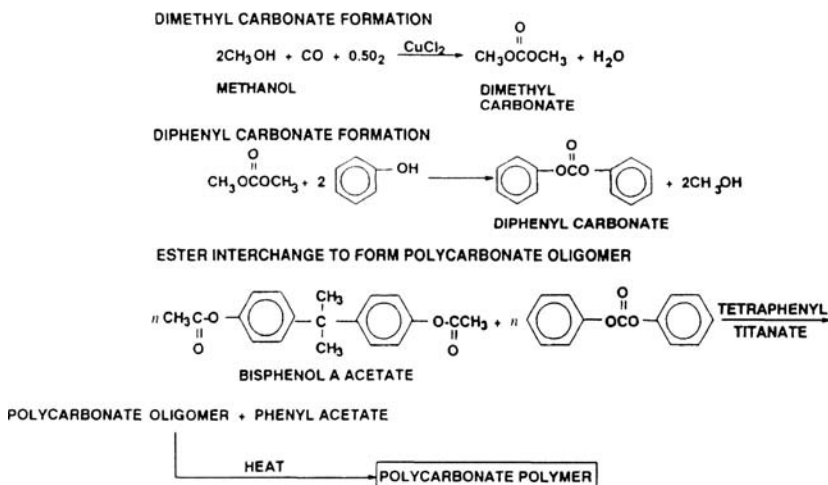


FIGURE 9.7 Preparation of polycarbonate resin without phosgene.

Diphenyl carbonate is used as the source of the carbonate linkage rather than dimethyl carbonate because the phenyl group is a much better leaving group.

Bayer and Ube are believed to use nitric oxide as a redox reagent in the synthesis of dimethyl carbonate. The chemistry of this approach involves the formation of methyl nitrite from methanol, nitric oxide, and oxygen. Methyl nitrite is subsequently reacted with carbon monoxide to give dimethyl carbonate together with nitric oxide for recycle. Asahi Chemical, in a joint venture with Chi Mei, have constructed a nonphosgene-based polycarbonate plant that pieces together two previously known reaction steps to make precursor dimethyl carbonate. The first step is the reaction of ethylene oxide with carbon dioxide in the presence of a catalytic amount of quaternary ammonium salts to give ethylene carbonate. The ethylene carbonate is then transesterified with methanol to give two products – dimethyl carbonate and ethylene glycol. Shell has also developed similar technology but based on propylene oxide in lieu of ethylene oxide.

Yet another approach for making dialkylcarbonates is via alcoholysis of urea. The tin-catalyzed reaction of methanol and urea is well known but suffers from low yields because intermediate methyl carbamate is prone to decompose to isocyanuric acid. Mitsubishi Gas Chemical has disclosed that reaction of urea with *n*-butyl alcohol works well and that di-*n*-butyl carbonate has an advantage over dimethyl carbonate when making diphenyl carbonate because it avoids the troublesome azeotropes that plague the separation of diphenyl carbonate and dimethyl carbonate.

A potential nonphosgene route is the oxidative carbonylation method, in which carbon monoxide and oxygen, together with a palladium catalyst, replace phosgene. Figure 9.8 summarizes the various approaches for making diphenyl carbonate.

The largest application for polycarbonates is in the electrical and electronics sector for compact disks, business machine enclosures, connectors and plugs, telephones, and electrical distribution devices. The second largest application is for window

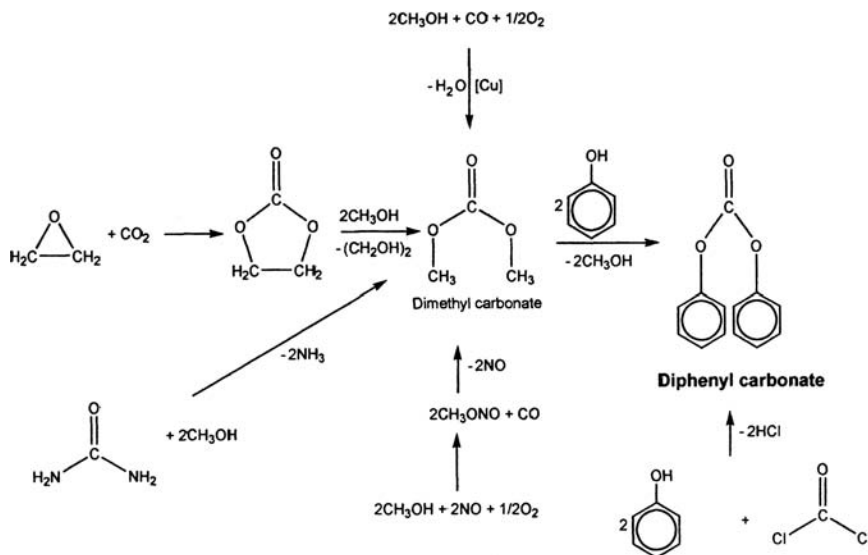
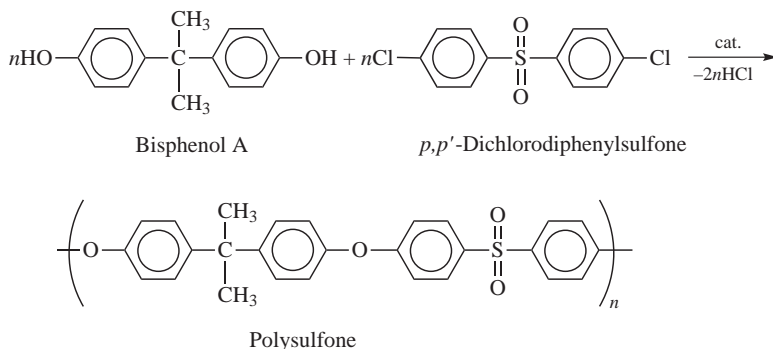


FIGURE 9.8 Routes to diphenyl carbonate.

glazing and related applications such as binoculars, where a virtually unbreakable molding with exceptional optical properties is required. Polycarbonates are also blended with poly(ethylene terephthalate) (Section 11.3.3) or poly(butylene terephthalate) (Section 11.3.4) to make impact resistant polymer alloys useful, for example, for automobile bumpers and even for side panels and doors.

9.1.2.3 Lesser Volume Uses for Bisphenol A

Bisphenol A is used in the synthesis of several engineering polymers because its stiffness contributes strength. The low volume polysulfone and polyether sulfone polymers require less than 3% of the bisphenol A produced. An example is the condensate of bisphenol A and *p,p'*-bis-chlorodiphenylsulfone. The hydrogen chloride produced in the condensation is neutralized with base as the reaction progresses.



These polymers are used in electrical, automotive, and electronics applications because of their thermal stability and excellent anticorrosive properties. Their superior corrosion resistance and stability to hydrolysis make them useful for medical instruments that require repeated sterilization. They are also used for ultrafiltration membranes in biotechnology and for the “Prism” separators by which hydrogen is separated from argon and nitrogen in a modification of the Haber process. The Haber process gives low yields of ammonia per pass, and much hydrogen and nitrogen must be recycled. The argon left from the air used in the synthesis gas manufacture accumulates (Section 12.5.1). To prevent an unacceptable level of argon, a purge was necessary, which removed nitrogen, argon, and also valuable hydrogen. This has to be used as fuel. The Monsanto process passes the recycled gases over a microporous polysulfone membrane. The hydrogen diffuses rapidly through the pores and is recycled without waste.

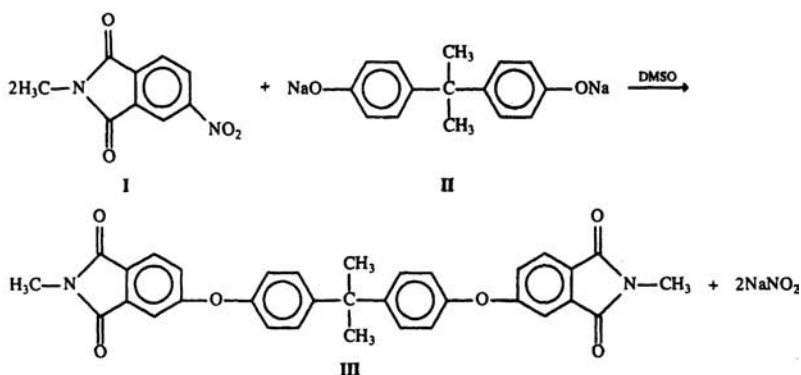
Polysulfone films can be made with reproducible properties and controllable pore size down to 40 nm. They can be fabricated into thin film composite membranes and are increasingly used for desalination by reverse osmosis. The problem with reverse osmosis is that membranes that are strong enough to withstand the pressures will permit only low flow rates. The problem is overcome by the use of skinned polysulfone membranes, in which a strong porous layer of polysulfone withstands the pressure and is coated with a thin semipermeable layer of polyimide polymer (Section 17.3). The world’s largest reverse osmosis plant opened in May 2010 at Hadera in Israel and produces 127 million cubic meters of water per year.⁹ Reverse osmosis is far less energy intensive than the various types of distillation. Given the forecast world water shortage, this is an important advance.

Improved membranes could reduce the operating costs of reverse osmosis plants. In 2010, Kraton Performance Polymers developed a block copolymer with separate regions that provide strength [poly(*t*-butyl styrene)], toughness and flexibility (ethylene–propylene copolymer), and water transport (styrene–sulfonated styrene). These so-called NEXARTM polymers are said to offer a water flux of up to 400 times higher than current reverse osmosis membranes. In a reverse osmosis plant they would save over 70% of membrane costs and approximately 50% of energy costs.¹⁰ Meanwhile, the improvement in reverse osmosis costs by adoption of the polysulfone membranes is remarkable. Desalinated water in Israel and Singapore in 1972 cost 50¢/m³, and this is still the cost in much devalued money.

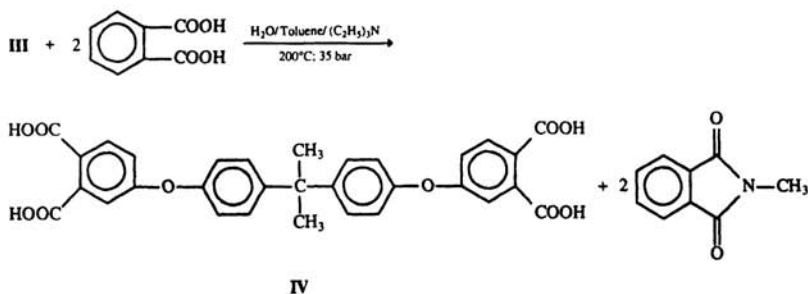
Produced in even smaller quantities than polysulfones are the polyarylates and the poly(ether imides). Polyarylates are condensates of bisphenol A with isophthalic and terephthalic acids. They have excellent resistance to ultraviolet radiation and good impact resistance. They are used in fog lamp lenses and to a larger degree in the rear tail lights of automobiles that are at eye level.

Poly(ether imides) (General Electric’s “Ultem”) have been designed to have some of the excellent properties of a polyimide but with greater tractability. They are condensates of *m*-phenylene diamine with a bisphenol-based dianhydride, made by a nucleophilic displacement between the sodium salt of bisphenol A (**I**) and *N*-methyl-4-nitrophthalic anhydride (**II**). The sequence of reactions is shown in Figure 9.9. Reaction 1 shows the formation of the bis(ether substituted phthalimide) (**III**).

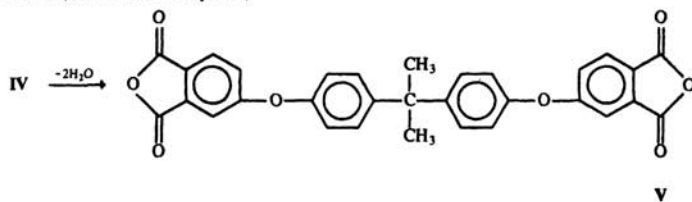
Reaction 1 [Formation of bis(ether substituted phthalimide)]



Reaction 2 [Formation of bis(ether phthalic acid)]



Reaction 3 (formation of dianhydride)



Reaction 4 [formation of poly(ether imide)]

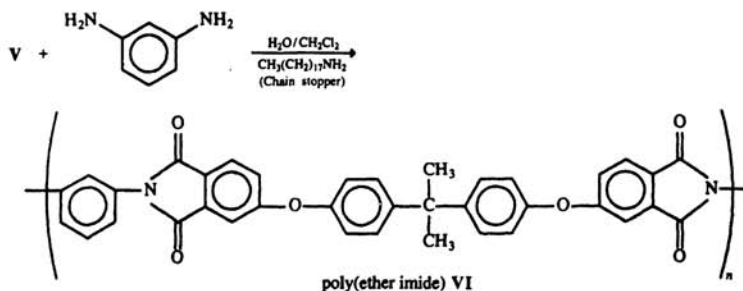


FIGURE 9.9 Preparation of a poly(ether imide).

Reaction 2 shows the displacement of the *N*-methyl-4-nitrophthalimide anhydride group by *ortho*-phthalic acid to give bis(ether phthalic acid) (IV) and reaction 3 shows the loss of water by this tetracarboxylic acid to give a dianhydride (V). Reaction 4 is the polymerization reaction of (V) with *meta*-phenylenediamine to give the polyimide (VI).

Bisphenol A is also the basis for a specialty corrosion-resistant, unsaturated polyester (Section 11.1.1) based on its reaction with phthalic and maleic anhydrides. Bromination of bisphenol A provides tetrabromobisphenol A, a flame retardant useful in its own right and as a monomer for flame retardant epoxy resins. As a halogenated organic, tetrabromobisphenol A is on the REACH list of substances of very high concern, and needs to conform to the RoHS (Restriction on Use of Hazardous Substances) regulations. It was banned in Holland in early 2001, but the industry hoped that it would escape the ban placed on many brominated flame retardants because it was not an additive to a polymer but an integral part of the polymer molecule and hence could not leach out. In June 2010, rather to the surprise of the environmentalists, the European Parliament Environment Committee opposed any restriction on the use of brominated fire retardants. This was a single event, however, and does not represent an agreed European Union position.

9.1.2.4 Environmental Problems

Bisphenol A has been under fire from environmental groups for many years but was ruled by the FDA to be safe. In March 2010, without retreating from its view, it was persuaded to add bisphenol A to its list of chemicals of concern. It has been shown to be an estrogen, affecting the endocrine system of animals, but was thought to be metabolized and excreted by humans and not to accumulate. This verdict still stands but has been challenged.¹¹ It is a matter of importance because bisphenol A resins are used in epoxy coatings for linings for food cans, and residual monomer may contaminate the food chain. Polycarbonate is also used for babies' bottles. Concentrations of residual bisphenol A in polycarbonates and epoxy resins are tiny, and the initial demand was only to ban them from babies' bottles. The FDA is to consider banning them also from food packaging, but consumer groups demand exclusion from all packaging.

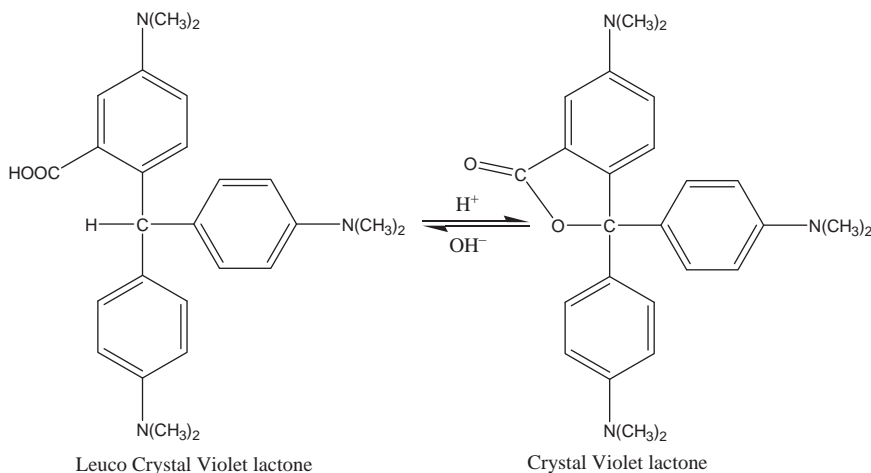
There is no obvious replacement for bisphenol A resins in linings for food cans, and those that have been proposed, such as the bis-epoxypropyl ester of isosorbide (Section 16.1.1), are more expensive. If cans are not properly protected, acid foods will attack the steel or aluminum, and higher pH or neutral foods may harbor the toxin-producing bacteria *Clostridium botulinus* or its relatives.

Meanwhile, Canada, Denmark, and France have banned the use of bisphenol A in bottles and other items that children may come in contact with. Some time ago, the European Food Safety Authority (EFSA) set a tolerable limit for bisphenol A consumption of 0.05 mg/kg of body weight and it has remained unchanged through 2010. The State of Oregon in the United States modified bisphenol A restrictions, so that young children may use bottles that contain it.

The issue, as with all environmental problems, is assessing whether bisphenol A poses a genuine hazard, what the expense of banning it would be, and what replacements are available.

A curious aspect of this is that bisphenol A is used in 60% of cash register receipts. They represent about 1.5% by weight of the receipts, and the chemical may be absorbed through the skin. The exposure is still well within EFSA's Tolerable Daily Intake, but shop assistants certainly ingest hundreds of times as much as users of polycarbonate bottles or customers. On the one hand, there are moves to change the thermal paper. On the other hand, study of the shop assistants should provide evidence of the toxicity or otherwise of bisphenol A.¹²

The chemistry by which the cash register receipts are printed is of interest. Leuco crystal violet, which coats the paper, is the colorless form of a triphenylmethyl dye, as shown below. When heated in the presence of electron acceptors such as phenols, in this case bisphenol A, it changes to the colored form and combines with four molecules of bisphenol A to give an intense dark-colored solid complex.¹³

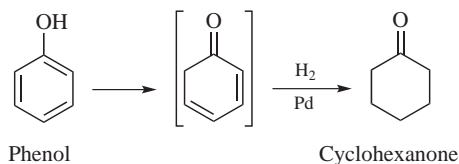


9.1.3 Cyclohexanone

The third largest use for phenol in both the United States and Western Europe is for caprolactam. The conversion of phenol to caprolactam is described in Section 9.2.2.

Approximately 33% of caprolactam comes from this source and the remainder from cyclohexane oxidation. The starting material for caprolactam is cyclohexanone, and this could come from phenol by a straightforward two-stage process in which the phenol is first hydrogenated to cyclohexanol and then dehydrogenated to cyclohexanone.

By a unique hydrogenation, however, phenol may be converted directly to cyclohexanone in high yield in a single step with a supported palladium catalyst at 12–13 bar and 200°C. Selectivity is about 97%:



Benzene is the starting material in the Asahi route (Section 9.1). It is selectively hydrogenated to cyclohexene, and the cyclohexene is converted to cyclohexanol by hydration. The cyclohexanol may then be oxidized or dehydrogenated to cyclohexanone. The key to the process is the ability to obtain high selectivity to the cyclohexene.

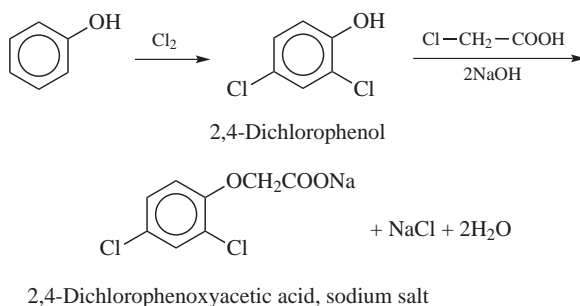
9.1.4 Alkylphenols

Phenol may be alkylated with olefins by a Friedel–Crafts reaction (Section 7.2.3) to provide alkylphenols. When alkylated with propylene trimer (Sections 4.9 and 6.3) nonylphenol results which, when reacted with ethylene oxide, provides an ethoxylate. This has been the most important surfactant for industrial detergents and has also been used in liquid dishwashing detergents. It has low foam properties and good detergency. Because of questions of biodegradability, however, it is being replaced by other surfactants including the more expensive ethoxylated fatty alcohols, alcohol sulfates, and alcohol ethoxysulfates. It is also converted to antioxidants for rubbers and plastics and for lube oil additives.

Octylphenol is made (Section 7.2.3) by alkylating phenol with diisobutene. Ethoxylation gives nonionic surface cleaners. Reaction with formaldehyde provides an oil-soluble phenolic resin. Dodecylphenol results from the condensation of propylene tetramer with phenol. Most of the product is used for lube oil additive formulations.

9.1.5 Chlorinated Phenols

The most important chlorinated phenol is 2,4-dichlorophenol, the raw material for the herbicide 2,4-dichlorophenoxyacetic acid or 2,4-D. It is the most widely used herbicide globally and the third most widely used in the United States.

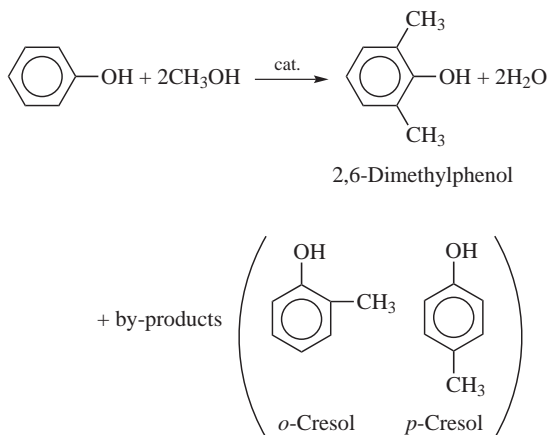


A mixture of 2,4-dichlorophenoxyacetic acid with 2,4,5-trichloroacetic acid (2,4,5-T) was manufactured primarily by Monsanto and Dow during the Vietnam War for the U.S. Department of Defense. It was known as Agent Orange because of the orange-striped barrels in which it was shipped. The 2,4,5-T was later discovered to be contaminated with the extremely toxic 2,3,7,8-tetrachlorodibenzodioxin, with well-known consequences.

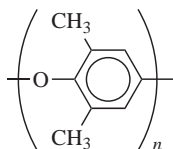
Pentachlorophenol, made by exhaustive chlorination of phenol, is a wood preservative and destroyer of slime. Like many other chlorinated compounds it has been outlawed in the United States because of its adverse environmental effects. The chlorine atoms make it highly lipophilic and, when it enters the body via the food chain, it accumulates in fatty tissue. The same is not true of 2,4-D, whose carboxyl group may facilitate its excretion.

9.1.6 2,6-Xylenol/Cresols

The synthesis of 2,6-xylenol (2,6-dimethylphenol) provides a small application for phenol. It is made by methylation of phenol at about 500°C at almost atmospheric pressure with a methanol:phenol molar ratio of 6:1 and a catalyst comprising magnesium oxide on an inert carrier pretreated with methanol vapor. Ten percent water provides continuous catalyst regeneration. *Ortho*- and *para*-cresol are by-products.



The xylenol is converted by oxidative coupling to poly(phenylene ether) whose recurring unit is



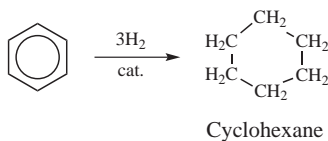
Ortho-cresol finds use in the manufacture of pesticides.

9.1.7 Aniline from Phenol

Aniline is normally prepared by the hydrogenation of nitrobenzene (Section 9.3). An alternative route involves the ammonolysis of phenol. Both of these processes are described in Section 9.3.

9.2 CYCLOHEXANE

Small quantities of cyclohexane are extracted from naphtha, but most is produced by hydrogenation of benzene. The process is operated in refinery complexes using hydrogen from catalytic reforming (Section 4.8). However, since the Clean Air Act reduced the permissible aromatics content in gasoline less hydrogen is available for such reactions.



Either nickel or platinum catalysts may be used, but both require benzene feed with a sulfur content of less than 1 part per million. Hydrogenation is carried out at an upper temperature of 230°C at 1.5–2.5 bar. Although liquid phase hydrogenations are more common, gas phase processes are available. These operate at temperatures as high as 600°C with moderate pressures of 25–50 bar.

Although some cyclohexane is used as a solvent, its major market is for the production of adipic acid and caprolactam.

9.2.1 Adipic Acid

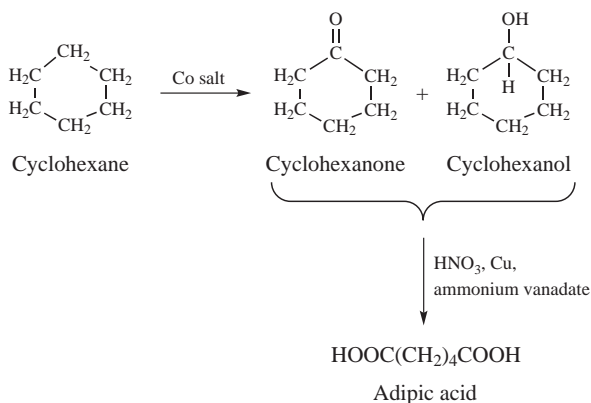
Benzene is the source of the two most important nylons, nylon 66 and nylon 6. Nylon 66 is the polymer formed when adipic acid condenses with hexamethylenediamine. Nylon 6 is the self-condensation product of caprolactam, which is the dehydration product of 6-aminocaproic (6-aminohexanoic) acid. The numbers used to designate nylons refer to the number of carbon atoms in the diamine and dibasic acid in that order. A single number indicates that the amino and carboxyl functions are in one molecule. Thus $[\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_4\text{CO}]_n$ is nylon 66, whereas $[\text{NH}(\text{CH}_2)_5\text{CO}]_n$ is nylon 6, and $[\text{NH}(\text{CH}_2)_6\text{NHCO}(\text{CH}_2)_8\text{CO}]_n$ is nylon 610, a specialty nylon made with sebacic rather than adipic acid.

In the early days of nylon, DuPont created a mystique about their product by advertising that it was made from coal, air, and water. Coal at that time was the source of the benzene or phenol feedstocks. Now both are derived from petroleum, and “made from petroleum, air, and water” does not sound nearly as good.

Nylon 66 and nylon 6 are interchangeable in most applications, but there are slight differences in properties. Nylon 66 has a slightly higher melting point and is

preferred for some engineering applications; nylon 6 offers better flexibility and oxygen barrier properties. Polyamide production in the United States in 2008 was 521,000 metric tons. Nylon 66 made up 50% of this with nylon 6 constituting 46% and 4% representing specialty polyamides. The corresponding figures in Western Europe were 53%, 46%, and 1%. In the United States, there is twice as much capacity for manufacturing nylon 66 as nylon 6. In Japan and China, however, nylon 6 is more popular. Many of the producers of caprolactam are fertilizer manufacturers who can use the by-product ammonium sulfate. Chinese caprolactam producers were subject to an antidumping tariff by the United States and a textile export quota was imposed by the European Union until 2008. Their elimination may alter the Chinese nylon 6 industry and consumption patterns in the West.¹⁴

The first step in the manufacture of the adipic acid needed for nylon 66 is the hydrogenation of benzene to cyclohexane. Thereafter the cyclohexane may be oxidized directly to adipic acid with nitric acid or with air over cobalt acetate, but yields are low, production of valueless by-products is high, and large amounts of nitric acid are consumed. Instead, a two-stage process is used. The initial oxidation at about 150°C and 10–15 bar over cobalt or manganese naphthenate or octanoate gives a cyclohexanol/cyclohexanone “mixed oil” or “KA oil” (ketone/alcohol oil). In the first stage of the reaction, cyclohexyl hydroperoxide forms and this is converted catalytically to the ol/one.



Conversions on the order of 10–12% are accepted in order to minimize the formation of adipic acid, which at this stage presents processing problems, and, more important, to minimize the degradation reactions that provide glutaric (C₅) and succinic (C₄) acids. The selectivity to the ol/one does not surpass 85%, but unreacted cyclohexane can be recycled. The desired ol/one mixture is purified by distillation.

The ratio of cyclohexanol/cyclohexanone may be increased from between 1:1 and 2:1 to about 9:1 by the addition of boric acid, which esterifies the “ol” as it is formed and prevents its further oxidation to cyclohexanone. The boric acid also increases the selectivity of the reaction. The cyclohexanol/cyclohexanone “mixed oil” is then oxidized to adipic acid with nitric acid at high selectivity, over a copper catalyst with

ammonium vanadate. Conversions per pass are on the order of 12%. No way of circumventing the use of nitric acid has yet been found, and this is the only example in industrial chemistry of the use of nitric acid as an oxidant for the production of a large volume chemical.

While nitric acid is an effective oxidizing agent for converting KA oil to adipic acid, an unavoidable by-product is nitrous oxide. For every kilogram of adipic acid, 0.32 kilogram of nitrous oxide is also produced. Nitric acid manufacture also produces 2.9 kg of nitrous oxide per 1000 kg of nitric acid, and together they were responsible in 2010 for about 10% of the 3.653 million metric tons of nitrous oxide emissions per year (equivalent to 701 million metric tons of carbon dioxide) in the developed world. Nitrous oxide is a “greenhouse” gas that is believed to contribute to global warming by absorbing reflected infrared radiation. It has been estimated that its warming potential is 310 times that of carbon dioxide. In addition nitrous oxide currently is the single most important ozone-depleting substance and is expected to remain the largest throughout the 21st century.

In 2010, it was estimated that adipic acid and nitric production contributed about 10.6% of all nitrous oxide emissions in the developed countries. Agriculture was responsible for 61.7%, vehicle emissions 12.8%, stationary fuel burning 6.2%, and manure management 8.8%.¹⁵ Human activity is thought to account for about 30% of nitrous oxide emissions and levels have risen by only about 13% over the past 200 years even though we have added so many more people. This makes the problem more rather than less difficult, even if the chemical industry is scarcely to blame.

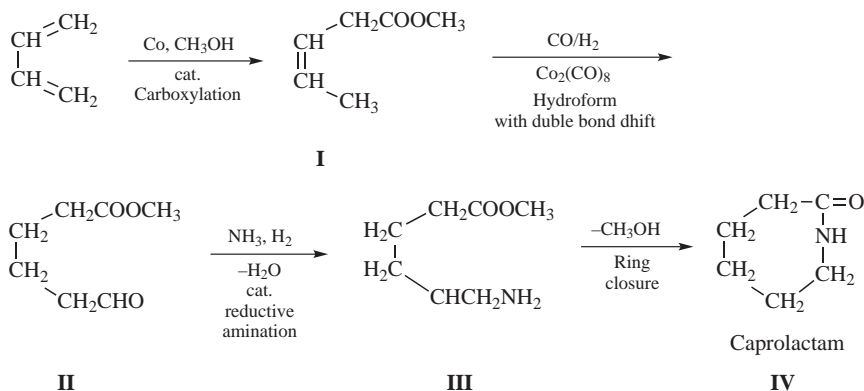
Most adipic acid producers now employ catalytic or thermal processes to destroy their nitrous oxide by-product, but Alsachimie has developed a process that converts it to nitric acid for recycle. This approach is of double benefit, as further nitrous oxide production from conventional nitric acid production is reduced. Solutia planned to avoid nitrous oxide emissions by using it in an adipic acid plant as an oxidant to convert benzene to phenol (Section 9.1).

Researchers have long sought another method of oxidizing cyclohexane to adipic acid, to avoid the cost of the nitric acid and to eliminate the environmental problems associated with nitrous oxide. In the 1960s, Halcon constructed a semiworks plant for Rohm and Haas that employed a two-stage air oxidation of cyclohexane. The second stage used a copper and magnesium catalyst in acetic acid solvent and gave an 80% yield based on KA oil. This was substantially less than the 93–95% yield achieved by conventional nitric acid oxidation and the approach was abandoned. In a 1994 patent application, BASF disclosed a catalyst system that was able to achieve selectivities of 88.2% to adipic acid, 6.2% to glutaric acid, and 3.6% to succinic acid. No plans for commercializing this process have been announced. Nagoya University researchers reported in 1998 that cyclohexane could be oxidized by hydrogen peroxide at over 90% selectivity by a phase transfer catalyst containing small amounts of tungsten.¹⁶

A number of noncyclohexane-based routes to adipic acid have been explored over the years. Most of them have been based on a butadiene feedstock. ARCO, BASF, Shell, DuPont, DSM, Idemitsu, and Rhone-Poulenc have all studied hydrocarbonylation of butadiene, which is typically performed in two stages in the presence of an alcohol, so that the end product is the corresponding dialkyl adipate. This is

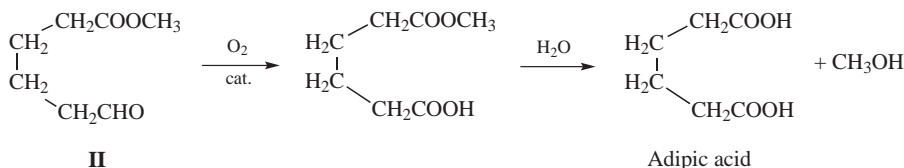
hydrolyzed to adipic acid, freeing the alcohol for recycle. In a joint 1998 patent, DuPont and DSM disclosed some promising results with a palladium, ferrocene, phosphorus-containing ligand catalyst system.

DuPont and DSM together developed another butadiene route to caprolactam called Altam. The first step, a carbonylation, is the same as the first step in BASF's adipic acid synthesis (Section 7.1.6.4) and gives methyl 3-pentenoate (**I**). This is hydroformylated with a cobalt catalyst rather than the more efficient rhodium catalyst because it shifts the double bond to the terminal position to provide the aldehyde (**II**). Reductive amination introduces an amine group to give an aminoester (**III**) and this cyclizes to caprolactam (**IV**) with the elimination of methanol.



DuPont withdrew, as they did from the two-for-one process in Section 7.1.5, prompted by their coincident withdrawal from the fibers business in 2003. Shell came in to help with catalyst development. The process is available for license but by 2008 there was no evidence it had been commercialized.

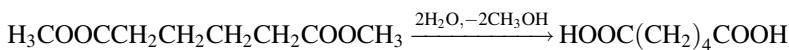
In 1998, DuPont and DSM disclosed a variation for the above reaction scheme in which compound **II** is oxidized to the half ester of adipic acid and then hydrolyzed to the free acid. Thus butadiene was converted to adipic acid by sequential reaction steps that included hydrocarboxylation, isomerization, hydroformylation, oxidation, and hydrolysis:



In a 1994 European patent, researchers at the University of North Carolina disclosed a means for dimerizing methyl acrylate to give a precursor that can easily be converted to dimethyl adipate by hydrogenolysis.¹⁷

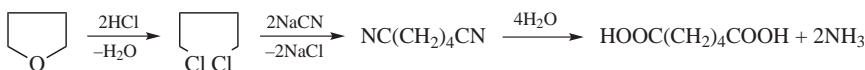


Methyl acrylate



Adipic acid

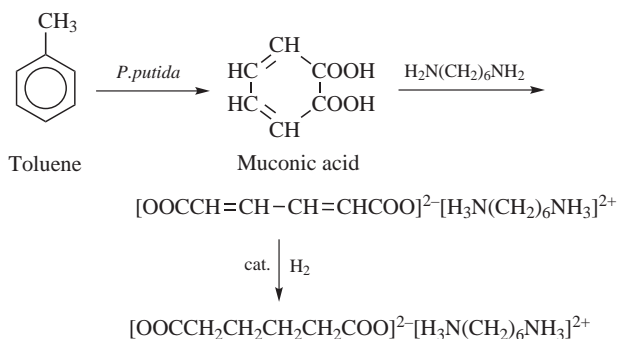
An obsolescent route to adipic acid starts with tetrahydrofuran (Sections 12.3.1 and 16.1):

Tetrahydrofuran 1,4-Dichloro-
butane

Adipic acid

The waste of chlorine, which does not appear in the end product, and the use of poisonous sodium cyanide make the process unattractive. Tetrahydrofuran was originally an agriculturally derived product obtained by hydrolysis of the pentosans in cereal hulls, primarily furfural. Today it is largely made from 1,4-butanediol or maleic anhydride (Section 12.3.1), although the furfural-based product is still produced and may become more significant as a renewable raw material.

A microbiological process for the production of adipic acid proposed by Celanese is not likely to be commercialized in the near future but is mentioned here because, like the microbiological process for propylene oxide (Section 6.8.1.5), it demonstrates the potential of modern biotechnology. Nylon 66 salt (an equimolar mixture of adipic acid and hexamethylenediamine) is produced from toluene via muconic acid. Toluene is first converted to muconic acid by a mutant strain of *Pseudomonas putida*.



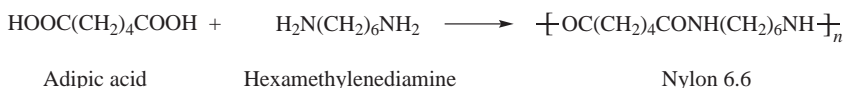
Muconic acid is much less soluble than adipic acid and is neutralized with hexamethylenediamine as it is formed in the fermenter to yield a solution of hexamethylene diammonium muconate in concentrations as high as 3.9%. This is separated from the cells by ultrafiltration. The salt may be precipitated by addition of isopropanol. Thereafter it is hydrogenated to give nylon salt for nylon preparation.

The key to the process is the ability to isolate the product from dilute aqueous solution without expensive removal of water by distillation or other means.

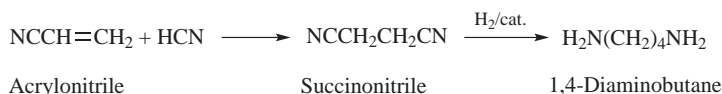
Nylon fiber accounts for 47% of the 2.8 million metric tons/year global market for adipic acid. Nylon resin accounts for 26%, and the remaining 27% is divided between polyurethanes (the largest), plasticizers, resins, coatings, and nylon 4,6.

9.2.1.1 Nylons from Adipic Acid

Once adipic acid has been made, it must be reacted with hexamethylenediamine, whose manufacture has already been described (Section 7.1.5) to obtain nylon 66.



Nylon 4,6 is another polyamide based on adipic acid, combined in this case with 1,4-diaminobutane. It is used as an engineering plastic rather than as a fiber. It has a higher melting point than either nylon 6,6 or nylon 6, with better toughness and temperature stability, but with the high water absorption that bedevils nylons. 1,4-Diaminobutane results from the addition of hydrocyanic acid to acrylonitrile to provide succinonitrile, which on hydrogenation gives the diamine. This is an excellent example of how to gain value from the HCN by-product from acrylonitrile production (Section 6.5).



The addition of HCN to the highly activated double bond of acrylonitrile takes place at 80°C in the presence of an alkaline catalyst such as triethylamine. The hydrogenation to 1,4-diaminobutane may take place with a cobalt oxide catalyst in a tetrahydrofuran solvent at 100°C and 190 bar.

Nylon raw materials cannot be made sufficiently pure to form a satisfactory polymer. Therefore the diamine and dicarboxylic acid are reacted at mild temperature to form a salt, which can be purified further by crystallization. Thereafter, the salt is heated further to polymerize it.

9.2.2 Caprolactam

There are many competing routes to caprolactam, summarized in Figure 9.10.¹⁸ The complexity of the possible routes and process decisions that have to be taken is astonishing. Meanwhile, the chemically significant routes are shown in Figure 9.11. In the initial and most widely used process, cyclohexanone is the starting material. The cyclohexanone component of “mixed oil” (Section 9.2.1) may be separated by

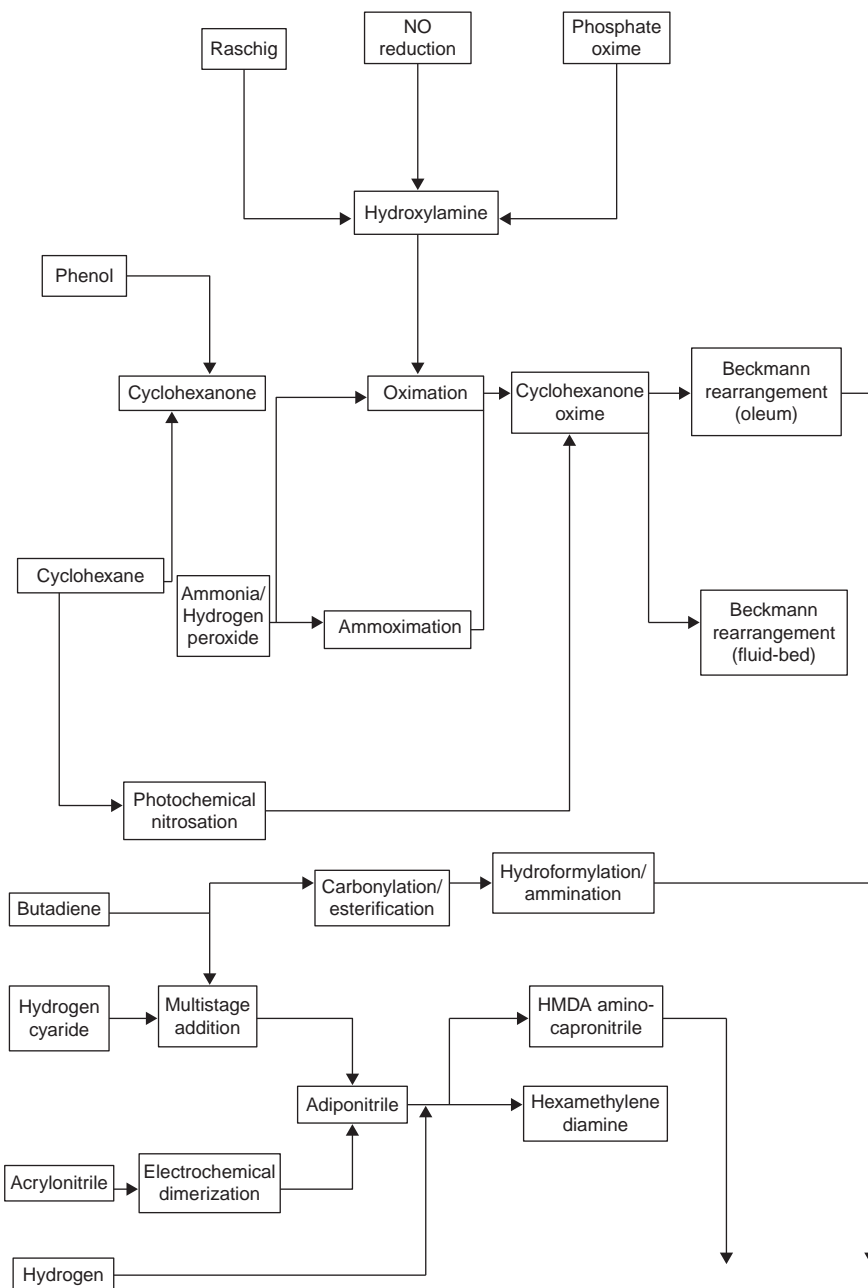


FIGURE 9.10 Routes to caprolactam. (Source: Nexant Inc.)

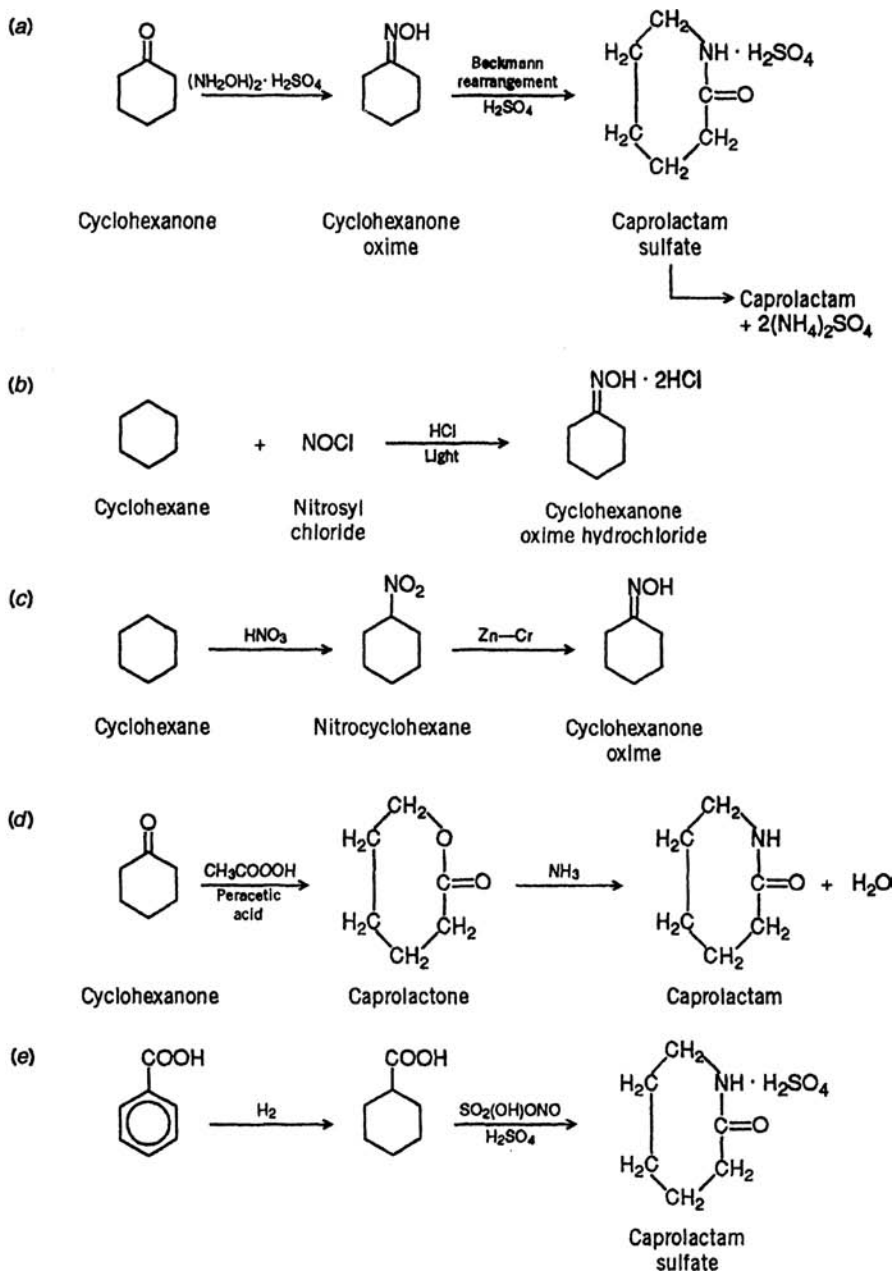
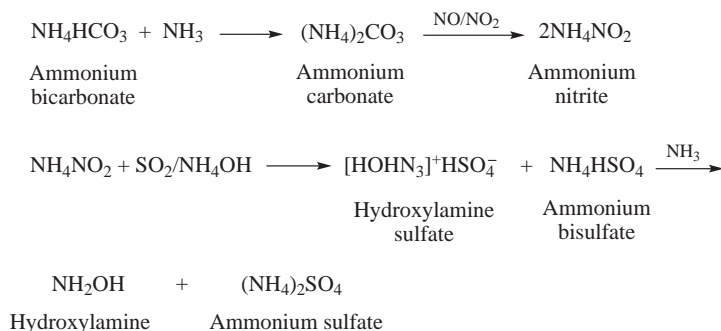


FIGURE 9.11 Significant routes to caprolactam.

distillation, the cyclohexanol may be dehydrogenated to cyclohexanone at 425°C and atmospheric pressure with metallic catalysts such as zinc or copper, and cyclohexanone may also be obtained from phenol (Section 9.1.3).

The cyclohexanone (Fig. 9.11a) reacts with hydroxylamine sulfate to give cyclohexanone oxime and sulfuric acid, which is converted to ammonium sulfate by the ammonia injected into the reaction mixture to drive the reaction to the right. Oximes undergo the Beckmann rearrangement, and this one is no exception; treatment with sulfuric acid gives caprolactam and ammonium sulfate.

The production of hydroxylamine also gives an ammonium sulfate by-product. Ammonium bicarbonate and ammonia give ammonium carbonate. Oxidation of ammonia gives an NO/NO₂ mixture that reacts with the carbonate to give ammonium nitrite for conversion with sulfur dioxide and ammonium hydroxide solution to hydroxylamine sulfate and ammonium sulfate.



Each kilogram of caprolactam produced generates 4.4 kg of ammonium sulfate by-product; 1.6 kg arises from the production of hydroxylamine sulfate, 1.1 kg from the production of the oxime, and 1.7 kg from the Beckmann rearrangement. This large amount of ammonium sulfate finds its way to the fertilizer market, particularly if a fertilizer plant is close to its source.

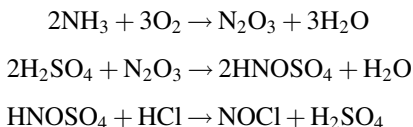
To add to these difficulties, hydroxylamine decomposes rapidly at room temperature, especially in the presence of atmospheric moisture and carbon dioxide. Ammonium nitrite is an explosive similar to the nitrate. In 1999 explosions wrecked the Nisshin Chemical plant in Japan and the Concept Sciences plant in Allentown, Pennsylvania, leaving BASF as the only producer by this process.¹⁹

The production of cumbersome amounts of unwanted ammonium sulfate stimulated the search for alternative methods for caprolactam production. One of them involves the use of phosphoric rather than sulfuric acid to effect the Beckmann rearrangement, because ammonium phosphate has greater value as a fertilizer.

A Japanese (Toray) process (Fig. 9.11b) involves treatment of cyclohexane with nitrosyl chloride and hydrogen chloride under actinic light (500 μm) to give the oxime hydrochloride without a Beckmann rearrangement.

The nitrosyl chloride is made in three steps. Ammonia is burned in air to nitrogen trioxide; the trioxide is absorbed in sulfuric acid to give nitrosylsulfuric acid;

hydrogen chloride is then added to the nitrosylsulfuric acid:



This process is wasteful of chlorine since the cyclohexanone oxime hydrochloride must be converted to the free oxime. On the other hand, the sulfuric acid that results in the NOCl reaction is recycled so that ammonium sulfate production is virtually eliminated. Nonetheless, it still results from the Beckmann rearrangement.

The major problem with photonitrosation is the engineering of an appropriate mercury light source. This same reaction is useful on cyclododecane (Section 7.1.6.2) to provide the monomer for nylon 12.

Another process (Fig. 9.11c), now largely of historical interest but used at one time by DuPont, involves liquid phase nitration of cyclohexane to nitrocyclohexane. This can be converted by careful reduction over a zinc–chromium catalyst to cyclohexanone oxime, the precursor of caprolactam. The manufacture of hydroxylamine is avoided, and about 66% of the ammonium sulfate is eliminated. The nitration step is akin to the gas phase nitration of propane to a mixture of nitroparaffins (Section 13.2) and is difficult to carry out in high selectivity.

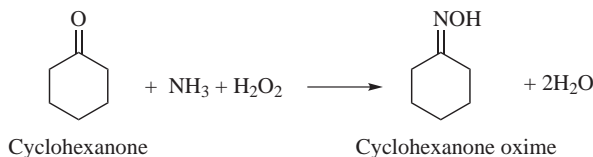
A fourth route to caprolactam (Fig. 9.11d) uses peracetic acid (from acetaldehyde and air) to convert cyclohexanone, at 50°C and atmospheric pressure, to caprolactone, which on reaction with ammonia provides caprolactam. Only the first step is now in use for the production of caprolactone.

A toluene-based route to caprolactam has been pioneered by Snia Viscosa. It was used in Italy until the early 1990s and is now used in China. Benzoic acid (Fig. 9.11e), prepared by the cobalt-catalyzed oxidation of toluene, is hydrogenated to hexahydrobenzoic acid, over a palladium catalyst at 170°C and 15 bar. This is treated with nitrosylsulfuric acid (see above) to obtain caprolactam sulfate. This process also eliminates 66% of the ammonium sulfate. In a variation of it, the caprolactam sulfate is diluted with water to dissociate the salt, after which the caprolactam is extracted from the 50% sulfuric acid solution with toluene or an alkylphenol. Thus the by-product is sulfuric acid rather than the salt. The acid can be pyrolyzed to sulfur dioxide for conversion via sulfur trioxide to concentrated sulfuric acid. This may be the most economical of all the processes.

A clever approach to the problem of eliminating ammonium sulfate formation is found in a DSM process in which a buffered solution of hydroxylamine reacts with cyclohexanone in solution to produce the oxime. The buffered hydroxylamine solution is produced by hydrogenation of nitrate ions to hydroxylamine in the presence of a phosphate buffer with a palladium catalyst. This solution reacts with cyclohexanone, and the oxime can be extracted with toluene. The aqueous solution can be recycled. DSM originally obtained caprolactam technology from Germany in lieu of reparations for World War II.

Several new caprolactam developments were announced in the mid-1990s and early 2000s. Some are discussed in Sections 7.1.5 and 9.2.1, but there were several others.

Enichem built a demonstration facility in 1994 that employed hydrogen peroxide to produce cyclohexanone oxime directly from ammonia and cyclohexanone.²⁰ Enichem refers to this reaction as “ammoximation.”



The elimination of the conventional steps for making hydroxylamine and converting it to the oxime reduce the capital expenditure and levels of ammonium sulfate by-product are lower.

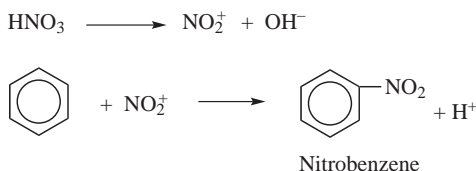
Sumitomo has developed a heterogeneous catalyst to carry out the Beckman rearrangement of cyclohexanone oxime to caprolactam in the gas phase (Fig. 9.11a). The catalyst is believed to be a metal-modified zeolite capable of withstanding the rigors of fluidization. The key benefit of this reaction step is the elimination of ammonium sulfate by-product. The process combines Enichem’s ammoximation of cyclohexanone with Sumitomo’s Beckman rearrangement, thus eliminating altogether the ammonium sulfate by-product.²¹ Sumitomo started this process in a 67,000 metric ton per year plant in Ehime, Japan, in 2003.

Of all these processes, only four were in use in 2010, the cyclohexanone-based process first described, the photonitrosation, the DSM process, and the Sumitomo/Enichem process.

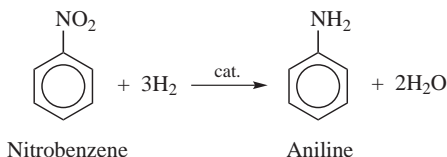
The many processes for caprolactam production nonetheless provide an example of the imagination that chemists bring to bear to solve a troublesome problem, in this instance the formation of large amounts of ammonium sulfate.

9.3 ANILINE

Next in line of benzene-based chemicals is aniline. Production in 2008 in the United States was 800,000 metric tons, 75% of which was used to produce isocyanates (Section 9.3.1). In the traditional process, benzene is first nitrated with mixed acids ($\text{H}_2\text{SO}_4/\text{HNO}_3$), which form a nitronium ion (NO_2^+) that attacks the benzene ring. The reaction is exothermic and the mixture must be cooled to maintain a temperature of about 50°C . An adiabatic process has been described, in which 65% rather than 98% sulfuric acid is used. The water in the acid absorbs the heat eliminating the need for external cooling. In the nitration of benzene, a small amount of *meta* isomer is obtained.



Nitrobenzene is reduced to aniline in almost quantitative yield by vapor phase hydrogenation at 270°C and 1.25 bar in a fluidized bed of a copper-on-silica catalyst. Also feasible is a vapor phase hydrogenation over a fixed bed of nickel sulfide on alumina.



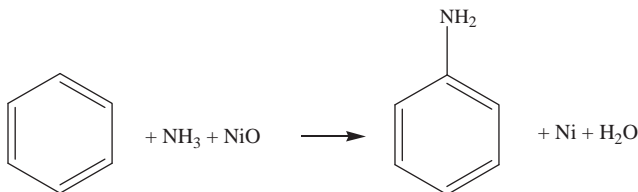
An older process employed iron turnings and hydrochloric acid as a source of hydrogen. This liquid phase process, in which the iron was converted to Fe_3O_4 , useful as a pigment, is little used today. Another process involving the ammonolysis of chlorobenzene was wasteful of chlorine and has not been used since 1967.

The newest method for aniline preparation involves the ammonolysis of phenol.

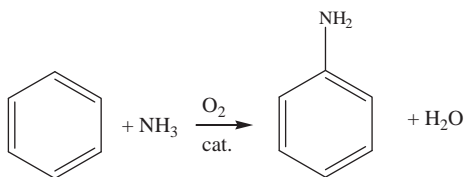


This reversible reaction is driven to the right by a high ammonia–phenol ratio, which also retards formation of diphenylamine. The reaction takes place at 200 bar and 425°C. The catalyst is proprietary, although initially a mixture of alumina and silica was proposed. Oxides of magnesium, aluminum, and tungsten are also effective in the presence of cocatalysts such as cerium and vanadium. Aniline selectivity is lower (about 90%) than in the nitrobenzene process, and diphenylamine and carbazole form as by-products by dehydrogenation. The lower capital cost of this process as compared to the nitrobenzene process is partly offset by higher raw material costs. On the other hand, the process eliminates ecological problems associated with the use of sulfuric and nitric acids.

The direct amination of benzene with ammonia via intermolecular dehydrogenation has been studied by DuPont but has never been commercialized, although much work has been done on the mechanism.²² Obviously such a process could provide the lowest possible raw material costs. The capital investment for the nitrobenzene section of a nitrobenzene–aniline plant is about 50% of the total, and its elimination would also reduce capital costs. The “cataloreactant,” a term apparently coined for this reaction, comprises nickel with small amounts of rare earth metal oxides together with a stoichiometric amount of nickel oxide, which reacts with the released hydrogen. The reaction takes place at 350°C and 290 bar with a high selectivity of 97% and a low conversion of 10% benzene per pass.

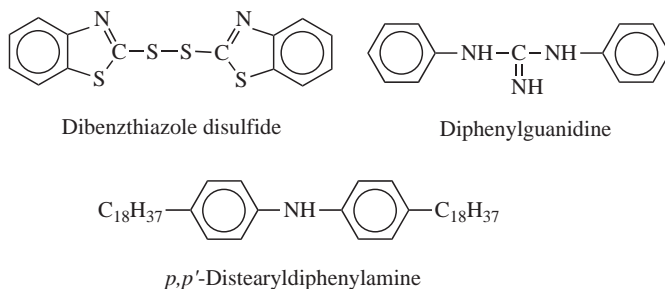


ICI reported a similar oxidative technique.²³



Selectivities as great as 96% are said to be attainable by use of a vanadium pentoxide on a γ -alumina catalyst that has been hydrogenated and in which the vanadium has an average oxidation state between four and five. It is similar to the $\text{V}_2\text{P}_2\text{O}_7$ catalysts used for maleic anhydride production (Section 7.4.2). Intermolecular dehydrogenations such as these are rare in organic chemistry. Another example is found in HCN preparation (Section 12.1), from ammonia and methane.

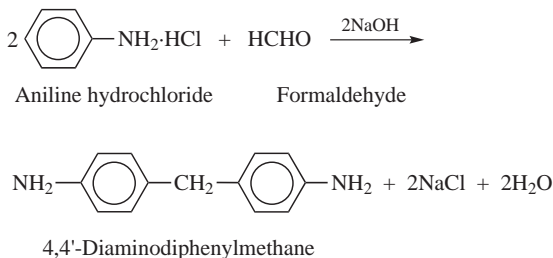
Aniline's major use is for conversion to 4,4'-diphenylmethane diisocyanate, discussed below. The second most important use is for rubber chemicals. Aniline is the basis for several rubber compounding agents. Thus dibenzthiazyl disulfide is a primary accelerator. Diphenylguanidine is a secondary accelerator and *p,p'*-distearyldiphenylamine is an antioxidant and ozone inhibitor.



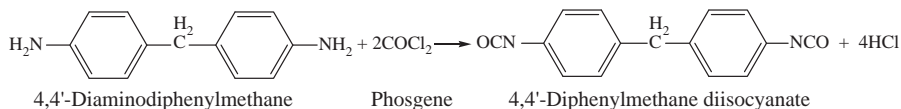
Aniline is also used as an intermediate for dyes, for drugs such as antihistamines (bamipine and thenaldine), in the synthesis of riboflavin, and for the preparation of hydroquinone (Section 9.7.1).

9.3.1 4,4'-Diphenylmethane Isocyanate

4,4'-Diphenylmethane diisocyanate (MDI, standing for methylene diphenyl diisocyanate) is the most important raw material for polyurethanes. U.S. production in 2008 was 98,000 metric tons. It is produced by the reaction of aniline hydrochloride with formaldehyde to form the 4,4'-, 2,4'- and 2,2'- isomers of diaminodiphenylmethane. The equation shows only the 4,4'-isomer:



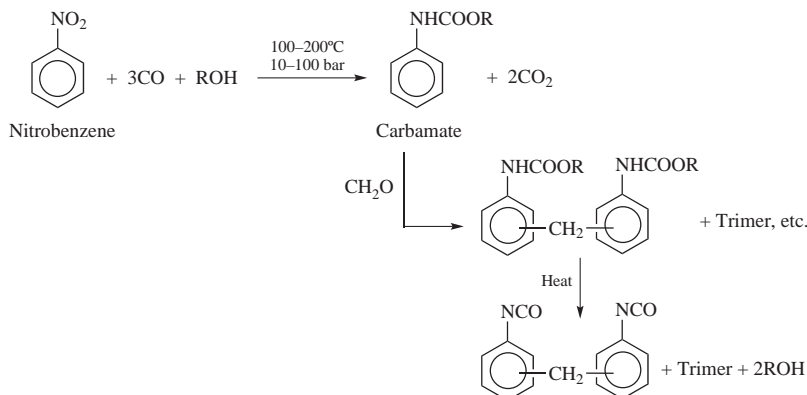
The diamine reacts with additional formaldehyde to give trimers, tetramers, and higher oligomers. The diisocyanate from the diamine is known as MDI whereas the isocyanate from the oligomers is known as poly MDI or PMDI. When MDI is required, the diamine is removed from the mixture by distillation and treated with phosgene:



Conversely, the entire mixture may be phosgenated and the MDI separated from the mixed isocyanates by distillation.

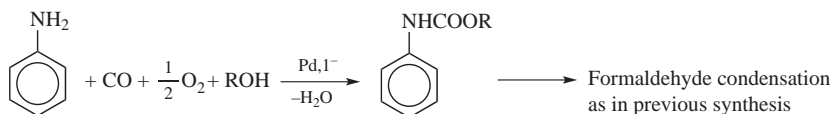
For the condensation of aniline and formaldehyde, aniline is treated with a stoichiometric amount of hydrochloric acid, and the hydrochloride is reacted with 37% formaldehyde for a few minutes at 70°C. The condensation is completed at 100–160°C for 1 hour. The mixture of di- and higher amines is recovered and phosgenated by reaction with phosgene in chlorobenzene solution. The carbamoyl chloride forms at 50–70°C and this is decomposed to the isocyanate at 90–130°C with release of HCl.

Phosgene is highly toxic – it was used as a poison gas in World War I. Hence several nonphosgene routes have been proposed for the preparation of MDI, but none has been commercialized. An ARCO process developed further by Japanese companies involves the direct carbonylation of nitrobenzene in the presence of a lower alcohol with a sulfur or selenium catalyst. A carbamate forms that can be reacted with formaldehyde to give dimers and oligomers, after which the carbamate groups are converted to isocyanates by heating with or without a catalyst. The recovered alcohol is recycled.

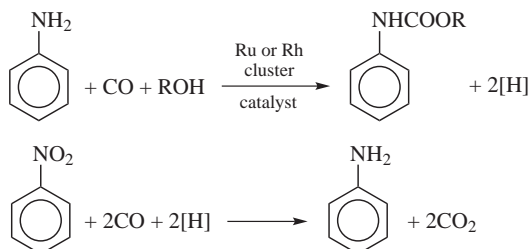


ARCO never commercialized the process, presumably because residual selenium could not be completely removed from the product. The catalysts proposed by the Japanese companies are said to be superior and include iodide-promoted palladium metal and a ruthenium carbonyl complex.

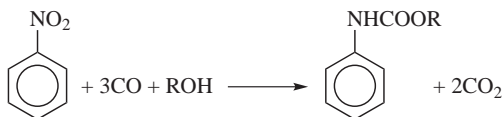
An Asahi process starts with aniline, which makes necessary an oxidative carbonylation. The catalyst is palladium metal with an iodide promoter. In this redox system, in which the palladium is catalytic rather than stoichiometric, Pd is reduced to Pd^{2+} and the iodide I^- is oxidized to iodine I_2 . Ethyl phenylcarbamate (phenylurthane) forms, which reacts with formaldehyde to give a dicarbamate, which in turn decomposes to the diisocyanate. An advantage of this process is that it is said to give a minimum of polymeric products in the formaldehyde condensation.



In a clever process developed by Catalytica Associates, Nippon Kokan, and Haldor Topsoe, a mixture of aniline and nitrobenzene is carbonylated in the presence of an alcohol to give methyl *N*-phenyl carbamate. Since oxygen is not present, the nascent hydrogen that forms reacts immediately with nitrobenzene to give aniline, which is further carbonylated.



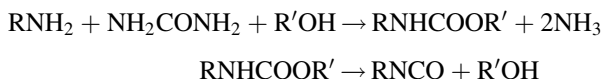
The overall reaction is



No net aniline need be supplied since the nitrobenzene is reduced to aniline in the process. A redox catalyst, which often leads to corrosion, is not required. Instead the process uses a cluster catalyst (an agglomeration of metal atoms) based on rhodium or ruthenium carbonyl complexes incorporating biphosphino or poly tertiary-amino ligands.

A number of other uncommercialized nonphosgene routes to methylene diphenyldicarbamate (MDC) appear in the literature. In one route²⁴ (middle of Fig. 9.12), aniline reacts with dimethyl carbonate to give methyl phenylcarbamate (MPC). MPC is then condensed to MDC which, as noted above, gives MDI on heating. A Chinese group²⁵ claims a direct route to MDC from aniline (bottom of Fig. 9.12) by treatment with dimethyl carbonate and formaldehyde in the presence of a silicotungstic acid/zirconia on silica dual function catalyst. Two other routes start with 4,4'-diaminodiphenylmethane (top of Fig. 9.12). This gives MDC on treatment with dimethyl carbonate or methyl carbamate.²⁶

Urea may also provide the CO for carbonylating the amine and a process of this type was commercialized in 1995 by Hüls for the manufacture of isophorone diisocyanate. An amine, urea, and an alcohol will form a carbamate, which can be converted to an isocyanate:



In the Hüls process, *n*-butanol is used for the alcohol. This type of chemistry seems to be effective only for aliphatic isocyanates and thus the challenge of making the large volume aromatic isocyanates without the use of phosgene still remains unmet.

Polyurethanes (Section 17.4.2) are made by reaction of diisocyanates with hydroxyl-containing compounds, primarily polyether polyols (Section 6.8.2). If the

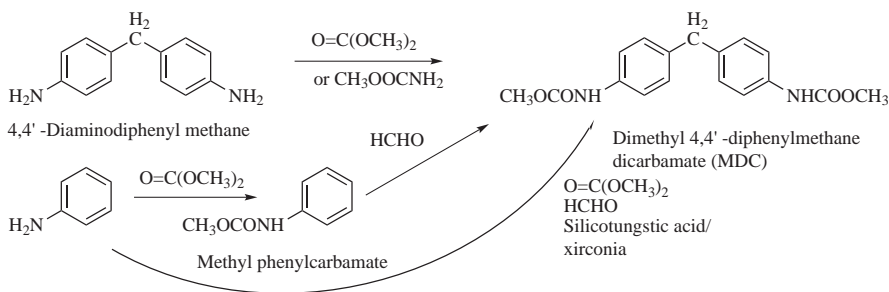


FIGURE 9.12 Some nonphosgene routes to MDC.

hydroxyl compound is bifunctional, a linear polymer results, but usually a polyfunctional alcohol is used to give a crosslinked, thermosetting resin. The polyols are sometimes replaced by polyamines. The products have a urea-type structure, and in industry these materials are commonly referred to as polyurethanes. The two major diisocyanates are MDI/PMDI and toluene diisocyanate (Section 10.3) and their application is primarily for foams. MDI/PMDI provides most of the rigid foams, which are largely used for insulation, whereas TDI provides the flexible ones, which are used in upholstery, bedding, and automobiles. A recent advance in insulation techniques is the use of polyurethane beads coated with reflective flakes of graphite.²⁷ The end-use pattern for MDI is shown in Figure 9.13. Of particular interest is RIM, an acronym for reaction injection molding. In this process, the isocyanate and a polyamine, which in this case reacts faster than a polyol, are pumped into a mold together with a catalyst, so that they may react in the mold. This makes large moldings possible. The steering wheels of cars are frequently made by RIM, because a skin forms that feels like leather.

There are also noncellular applications for isocyanates, mostly in corrosion-resistant maintenance coatings, which use primarily MDI/PMDI if yellowing is not a problem. Nonyellowing urethane coatings are based on aliphatic isocyanates derived from hexamethylenediamine, bis-aminocyclohexylmethane, “isophorone diamine,” xylylenediamine, and tetramethylxylylene diisocyanate. These are all termed aliphatic, even though two of them contain aromatic rings. The isocyanate groups, however, are attached to aliphatic carbon atoms. The structures are shown in Figure 9.14.

Nonyellowing isocyanates are useful for aircraft topcoats over epoxy primers. A more recent application, which could develop into large volume usage, is clear automotive top coating.

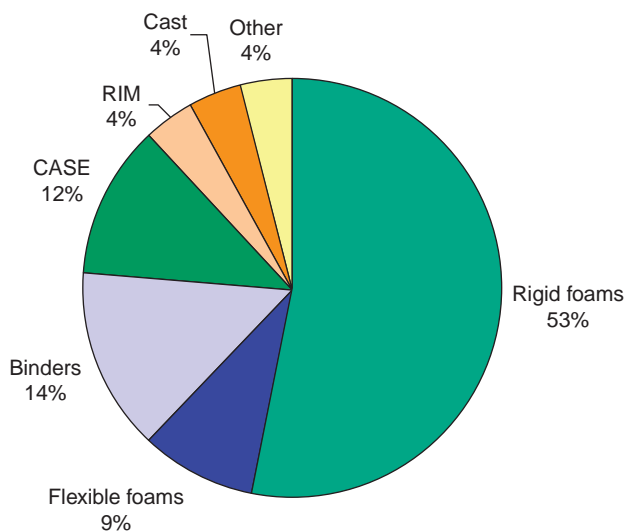
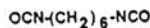
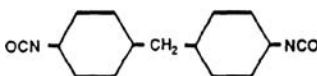


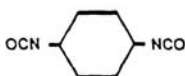
FIGURE 9.13 MDI end-use profile (United States, 2008).



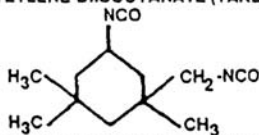
HEXAMETHYLENE DIISOCYANATE (SEVERAL PRODUCERS)



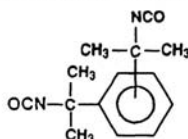
METHYLENE BIS-CYCLOHEXYL DIISOCYANATE (BAYER)

*trans*-1,4 - CYCLOHEXANE DIISOCYANATE (AKZO)

XYLYLENE DIISOCYANATE (TAKEDA)



ISOPHORONE DIISOCYANATE (SEVERAL PRODUCERS)

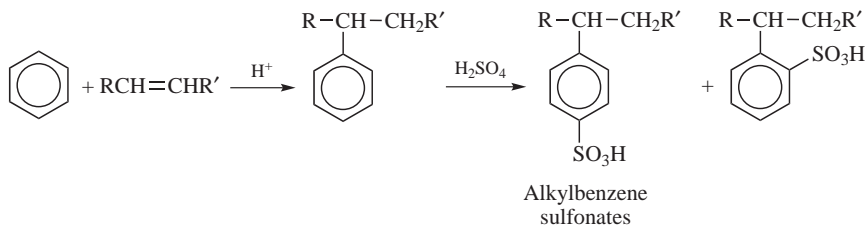


TETRAMETHYL XYLYLENE DIISOCYANATE (CYTEC)

FIGURE 9.14 Selected “aliphatic” diisocyanates.

9.4 ALKYLBENZENES

The most important alkylbenzenes are those with C_{10} – C_{14} side chains. These are sulfonated to provide alkylbenzenesulfonate surfactants, useful in detergent formulations, and have applications in plasticizers, lubricating oil additives, and polymerization modifiers. The equation is written for an internal olefin:



There are several sources of the side chains for the Friedel–Crafts alkylation of benzene for surfactants. Initially propylene tetramer, from polygas (Section 4.9), a highly branched dodecene, was used and is said still to be used in developing countries. In the United States and Western Europe, it has been outlawed because branched chain surfactants biodegrade very slowly, with resultant foaming in rivers and sewage plants.

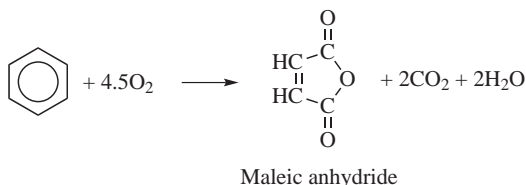
The move to biodegradable detergents made necessary the manufacture of linear olefins. High molecular weight paraffins (C_{20} – C_{30}), which occur in the wax separated from lubricating oil, can be separated into linear and branched molecules by use of molecular sieves, particularly by UOP's Molex process. The linear fraction can then be steam cracked, just as lower hydrocarbons can, to provide α -olefins with both even and odd numbers of carbon atoms with chain lengths varying from C_6 to C_{18} . These are impure but suitable for surfactants. Alternatively, paraffins from C_6 to C_{19} may be dehydrogenated catalytically to internal olefins.

The Friedel–Crafts alkylation of benzene can also be carried out with alkyl chlorides (monochloroparaffins) made by chlorinating *n*-alkanes with 10–15 carbon atoms. Third, dehydrochlorination of the monochloroparaffins provides useful olefins. The supply of wax, however, is limited, which makes necessary the use of olefins from ethylene oligomerization (Section 5.3). Either linear or internal olefins with chain lengths of C_{10} – C_{13} can be used, the major source of the latter being the Shell SHOP process (Section 5.3.4). From internal olefins, as in the equation above, a molecule with two side chains results, but since both of these are linear they are biodegradable.

The Friedel–Crafts alkylations were traditionally brought about by hydrogen fluoride or aluminum chloride catalysts. These are noxious and have largely been replaced by solid acid catalysts such as zeolites, certain synthetic clays, and solid Lewis acids.

9.5 MALEIC ANHYDRIDE

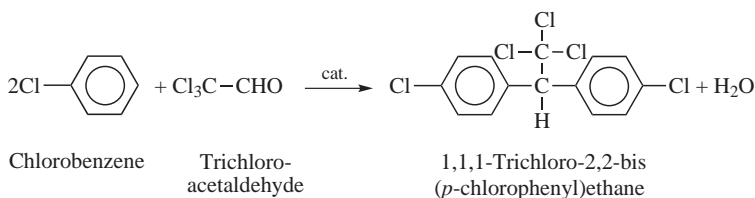
Most maleic anhydride is made by the oxidation of butane or, less frequently, 1- and 2-butenes (Section 7.4.2). An older method is based on the oxidation of benzene and in 2006 was still used in a few small European plants. It is analogous to the process for phthalic anhydride from naphthalene (Sections 11.1 and 14.1). The vapor phase oxidation is carried out with a supported vanadium pentoxide catalyst at 400°C . A mixture of maleic acid and maleic anhydride results, and the acid may be dehydrated to the anhydride directly without separation. The product is purified by batch vacuum distillation. The uses for maleic anhydride were described in Section 7.4.2.



9.6 CHLORINATED BENZENES

Chlorobenzene results from the liquid phase chlorination of benzene at slightly above room temperature with a ferric chloride catalyst. Small amounts of di- and trichlorobenzene form. Oxychlorination achieves the same result (Section 5.4) with hydrogen chloride and air instead of chlorine, and an alumina-supported cupric chloride–ferric chloride catalyst. This was in fact the first use for oxychlorination, which today makes a key contribution to vinyl chloride manufacture. Conversion is kept at 10–15% to suppress the formation of di- and polychlorobenzenes and to control the reaction's exothermicity.

Chlorobenzene is used primarily as a solvent (cf. reaction of 4,4'-diaminodiphenylmethane with phosgene, Section 9.3.1). It may be converted to aniline (Section 9.3) and has been used in the past as a raw material for phenol (Section 9.1). Chlorobenzene condenses with trichloroacetaldehyde (chloral) to yield the insecticide bis(chlorophenyl) trichloromethylmethane (DDT). In about 80% of the product the chlorines are *para-para* but *ortho-para* and *ortho-ortho* forms are also produced.

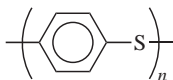


DDT was remarkably effective in mosquito control but was banned because its stability and lipophilicity caused it to accumulate in body fat. Strains of mosquitoes immune to DDT have emerged, either because they have developed enzymes that hydrolyze DDT, or because natural selection has retained only immune strains. In many areas DDT is now useless, and there was a drive to ban it completely at the United Nations Environment Program negotiations on persistent organic pollutants in Johannesburg in 2000.²⁸ There are, however, places where it remains effective, and it is still used in India, North Korea, and probably various other countries in Africa, Asia, and South America. Global usage, which peaked in 1963 at 82,000 metric tons per year, had dropped to 3314 metric tons by 2009. India is the only country still manufacturing DDT, China having ceased production in 2007. In most cases, its use is restricted to spraying the insides of houses to limit malaria. In spite of support for the ban from the major environmental groups, the threat of even more deaths from malaria resulted in a treaty permitting its restricted use in disease vector control.

Dichlorobenzenes are small-volume chemicals which, like many chlorine derivatives, are being phased out. *para*-Dichlorobenzene is used as a moth

repellant and as the deodorant in toilet blocks. It is made by direct chlorination of benzene over a ferric chloride catalyst. The 1,2-isomer is the principal by-product. The reaction mixture may be purified by fractional crystallization, based on the fact that *para*-dichlorobenzene melts at 53.5°C while its isomers, together with chlorobenzene, all melt below 0°C. *para*-Dichlorobenzene has an unpleasant odor and is supposed to be handled with gloves and used only in enclosed containers and not outdoors. From time to time, various safety agencies around the world have claimed it to be carcinogenic and have banned it, but the evidence is not conclusive.²⁹ About 2300 metric tons per year are made in the United States, and it is sold mainly to households, raising the question as to how far the safety regulations are observed. The big museums avoid chemical moth repellants and, instead, hire freezer vans once a year and kill moth larvae cryogenically. Meanwhile, few cases of toxic reactions are reported, and there are few replacements available; indeed *para*-dichlorobenzene is probably less toxic than naphthalene, the other traditional moth repellant.

para-Dichlorobenzene reacts with sodium sulfide; the specialty polymer, poly(phenylene sulfide) results. Its recurring unit is

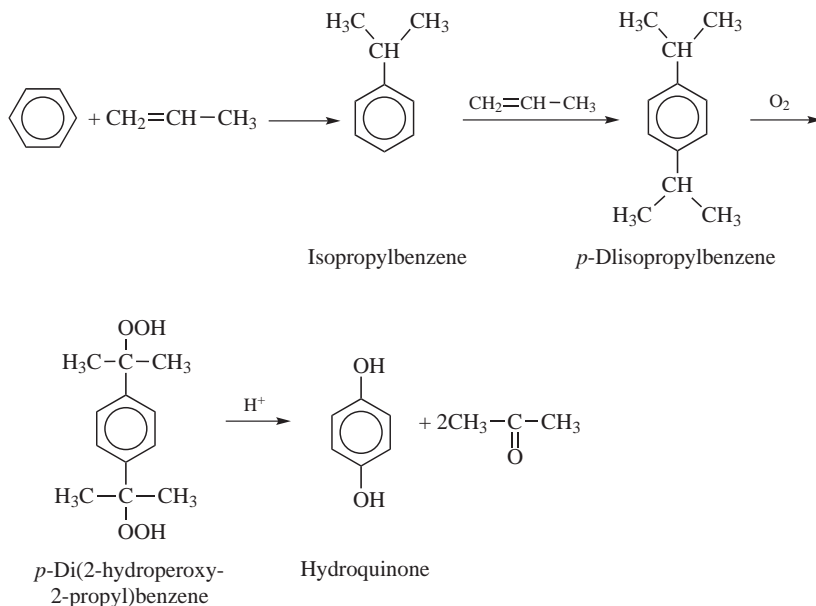


ortho-Dichlorobenzene is a solvent for toluene diisocyanate.

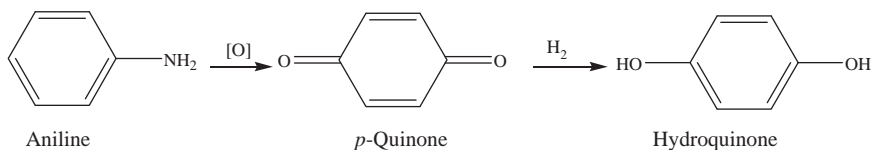
9.7 DIHYDROXYBENZENES

9.7.1 Hydroquinone

Of the three dihydroxybenzenes – hydroquinone, resorcinol, and catechol – hydroquinone is the most important. Numerous processes have been proposed for its preparation. One is analogous to the cumene-based phenol process (Section 6.6). *para*-Diisopropylbenzene is prepared by alkylating cumene with isopropyl chloride in the presence of aluminum chloride at 90°C to achieve a 98% molar yield. Peroxidation takes place at 90–100°C with air in the presence of dilute sodium carbonate. A mixture of mono- and dihydroperoxides results. Extraction with aqueous alkali separates the two. The oxidation gives 10% conversion and the ultimate molar yield of dihydroperoxide is 65%. It is decomposed in acetone solution with dilute sulfuric acid at 90°C and 2 bar. Hydroquinone is formed in an overall yield of 60 mol %. Acetone is a coproduct. Dihydroperoxides are highly unstable, and the original pilot plant, in Hull, United Kingdom, blew up, but plants now operate in the United States, Europe, and Japan.

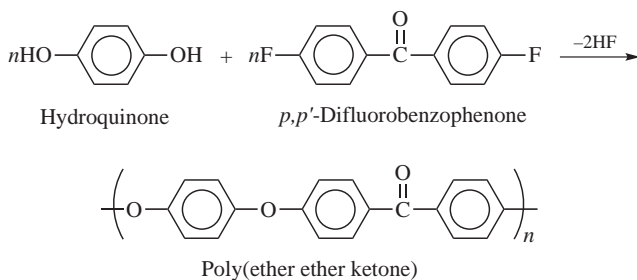


The earliest procedure for hydroquinone manufacture is still widely used, although it is not ecologically attractive. Aniline is oxidized by manganese or chromic oxides in acid solution to *p*-quinone. Reduction of the quinone with iron and sulfuric acid provides hydroquinone and ferrous sulfate, which can subsequently be converted to ferric oxide, useful as a pigment but whose consumption is declining.



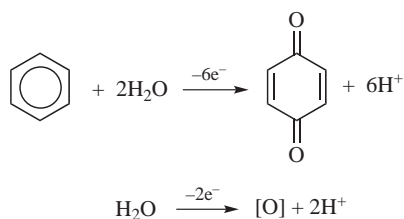
The initial oxidation is carried out below 10°C . Chromic acid may be used instead of manganese dioxide. In either instance, ammonium sulfate residues provide a disposal problem.

Hydroquinone is used as a component of a high performance plastic, poly(ether ether ketone) (PEEK), a condensate of hydroquinone and *para*, *para'*-difluorobenzophenone.

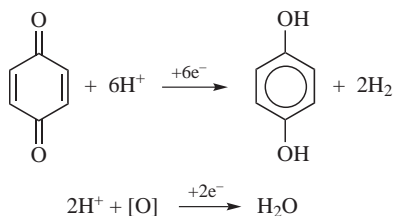


The electrolytic oxidation of benzene to hydroquinone has never been commercialized although it appears attractive economically and has been piloted several times. The benzene is oxidized continuously at the anode of an electrolytic cell to produce benzoquinone, which is concurrently reduced to hydroquinone at the cathode.

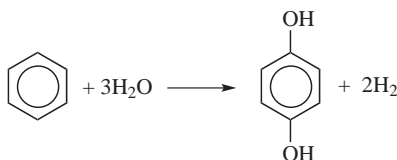
Anode



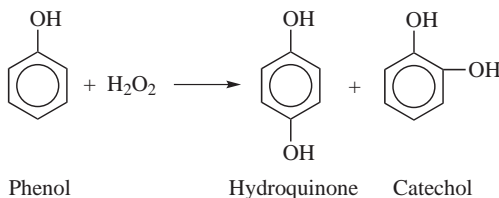
Cathode



Overall

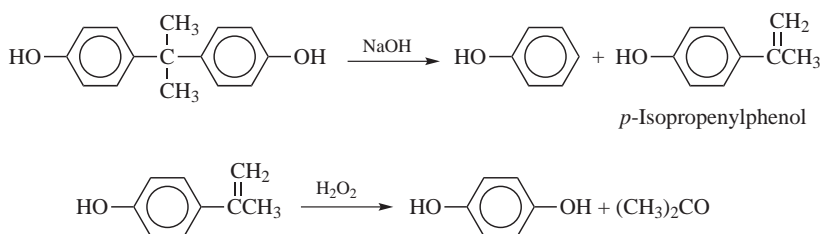


The direct hydroxylation of phenol with hydrogen peroxide in the presence of iron and cobalt salt catalysts provides a mixture of catechol and hydroquinone (Sections 9.7.1 and 9.7.3).

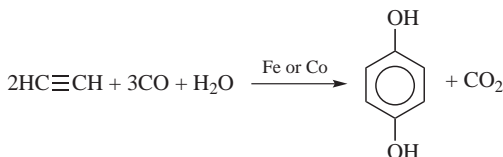


A similar process involves oxidation of phenol with percarboxylic acids or mixtures of hydrogen peroxide with phosphoric or perchloric acids at 90°C. Rhone-Poulenc and Ube Industries operate plants.

A process based on bisphenol A involves its conversion to *para*-isopropenylphenol either by a base-catalyzed or thermal decomposition. Reaction of *para*-isopropenylphenol with hydrogen peroxide yields hydroquinone and acetone.



A Reppe process involves simultaneous cyclization and carbonylation of acetylene with iron or cobalt catalysts. A more modern version makes use of ruthenium or rhenium catalysts at 600–900 bar with hydrogen instead of water. If carbonyl cluster catalysts are used lower pressures are possible at temperatures of 100–300°C. These processes have not been commercialized, probably because of difficulties in recovering the precious metal catalysts.



A biological route to hydroquinone and benzoquinone is described in the literature.³⁰

The major uses for hydroquinone are as an antioxidant and ozone inhibitor in rubber manufacture. It is also a polymerization inhibitor in the manufacture and storage of monomers such as acrylonitrile, vinyl acetate, and acrylic and methacrylic esters. It is a precursor of butylated hydroxyanisole (BHA), a food grade antioxidant prepared by alkylating the monomethyl ether of hydroquinone with isobutene.

A related food grade antioxidant is butylated hydroxytoluene (BHT) (Section 7.2.6). Growth in hydroquinone usage is not expected because tires last longer and the advent of digital cameras has almost destroyed the photographic market that formerly was hydroquinone's main outlet.

9.7.2 Resorcinol

Resorcinol is made by benzene disulfonation analogous to an obsolete process for phenol manufacture (Section 9.1). Koppers (now Indspec) is the only U.S. producer, and Hoechst closed the last European plant in 1992. Isomers are avoided because of the *meta* directiveness of the sulfonic acid group. Monosulfonation is carried out at 100°C with 100% sulfuric acid made by adding oleum to 96% acid (Fig. 9.15). Oleum is used at 80°C for the second sulfonation, because the water produced dilutes the acid

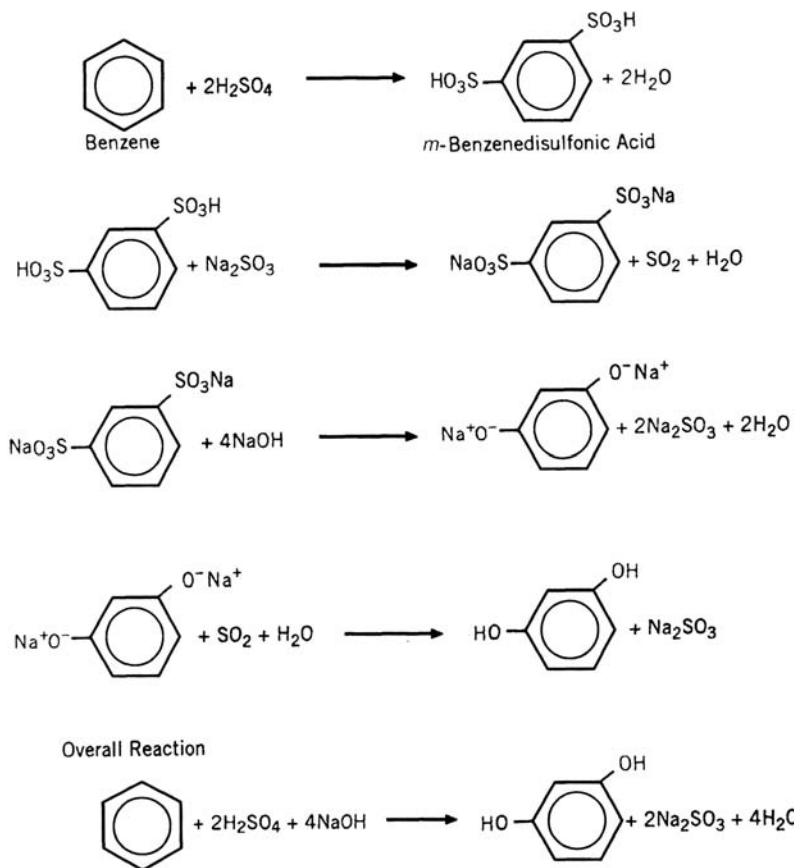


FIGURE 9.15 Resorcinol from benzene.

and, if the strength drops below 80%, sulfonation ceases. The disulfonic acid is neutralized with sodium sulfite or sodium carbonate to produce SO_2 or CO_2 . Sodium sulfite is preferred because it is a by-product of the overall reaction and can be recycled.

Sodium sulfate is also formed as a by-product because excess sulfuric acid is used, which must be neutralized. A variation of the neutralization step, which eliminates the excess sulfuric acid, involves the use of calcium carbonate to complete the 90% neutralization achieved with sodium sulfite. A 9:1 mixture of sodium and calcium salts of the benzenedisulfonic acid is obtained, which is further treated with sodium carbonate. The sodium displaces the calcium and produces calcium carbonate together with the completely neutralized sodium salt of benzenedisulfonic acid.

This sodium salt is fused with sodium hydroxide in a batch process at 300°C at a 4 to 1 molar ratio of caustic to sodium salt. The resulting mixture is neutralized either with sulfuric acid or with the SO_2 evolved in the initial neutralization of the benzenedisulfonic acid. A mixture of resorcinol, sodium sulfate, and sodium sulfite results. Resorcinol may be extracted from the aqueous solution by several solvents including isopropyl ether.

The alternative process is analogous to the *p*-diisopropylbenzene route to hydroquinone (above). *m*-Diisopropylbenzene is oxidized to its dihydroperoxide and this is cleaved with acid to resorcinol and acetone. There are far more by-products than in the cumene-phenol process and the rate of reaction is slower, but Sumitomo is said to operate a plant in Japan.

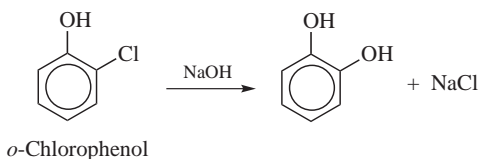
Resorcinol is used in the formulation of high performance adhesives; primarily resorcinol-formaldehyde condensates, for the rubber and wood product industries and for bonding tire cord to the rubber tire matrix. These adhesives have better properties than phenol-formaldehyde resins (Section 9.1.1) for the production of laminated beams where high strength is required and the application of heat is impractical. Resorcinol is also a raw material for the production of pharmaceuticals, dyes, and ultraviolet absorbers. Typical is its conversion to *meta*-aminophenol by reaction with ammonia, a reaction analogous to the amination of phenol to aniline (Section 9.3).

The lead salt of mononitroresorcinol is made by mild nitration of resorcinol. It is used in modern firework displays, often set to music, where split second timing of ignition is essential.³¹ It is one of the few explosives capable of igniting reliably when a "bridge wire" running through it glows transiently red hot when an electric current is switched on. It produces a flame that burns for about 4 milliseconds, depending on the applied current, and is used with more conventional oxidizers and fuels.

9.7.3 Catechol

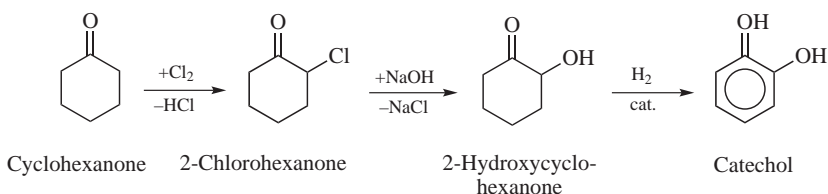
ortho-Dihydroxybenzene (catechol or pyrocatechol) results from the caustic hydrolysis of *ortho*-chlorophenol in the presence of copper powder at $190\text{--}230^\circ\text{C}$ and 3–6 bar. In the process, a chlorine atom is replaced by a hydroxyl group.

Conversion is 69%, of which 89% is catechol, and 11% resorcinol and higher phenols. The process is no longer used commercially.

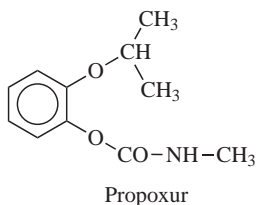


The preferred route involves the direct hydroxylation of phenol with hydrogen peroxide in the presence of formic and phosphoric acids. A mixture of catechol and hydroquinone results in a ratio of 3:2. Formic acid alone favors increased formation of hydroquinone. The two products are separated by distillation. The process is believed to be used in Italy and Japan.

A third synthesis involves the chlorination of cyclohexanone to 2-chlorocyclohexanone. Caustic hydrolysis of the chlorine provides 2-hydroxycyclohexanone, which can then be dehydrogenated to catechol.



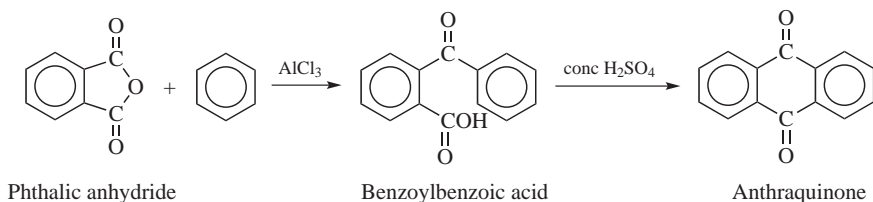
The major use for catechol is for the preparation of a carbamate insecticide, propoxur, used to kill household pests. It is toxic to honeybees and is potentially toxic to children who are chronically exposed to it. The U.S. Environmental Protection Agency is therefore unwilling to allow its indoor use against bedbugs.



9.8 ANTHRAQUINONE

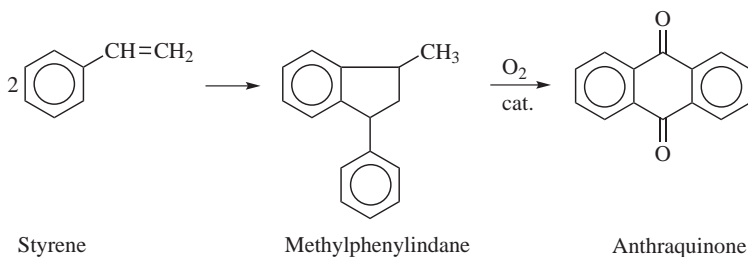
The Friedel–Crafts condensation of benzene and phthalic anhydride (Section 9.1) in the presence of aluminum chloride at 25–60°C produces benzoylbenzoic acid.

The product is cyclized with oleum to anthraquinone, which is purified by sublimation at 380°C. Yields are of the order of 95%.



A second route to anthraquinone involves the direct oxidation of anthracene, a process still practiced in Europe, where high purity anthracene has traditionally been available from coal tar fractionation.

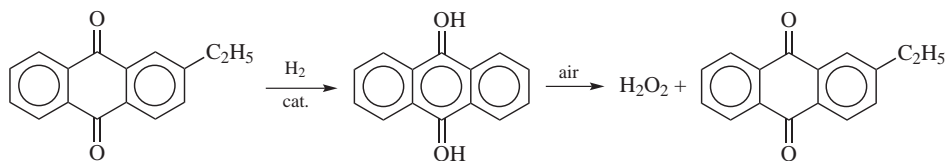
In a third process, styrene is dimerized to methylphenylindane, which can be oxidized in the vapor phase to anthraquinone. The dimerization is catalyzed by sulfuric acid at reflux temperature. The complex vapor phase conversion to anthraquinone takes place over a promoted vanadium pentoxide catalyst.



Anthraquinone has been used primarily for the production of dyes and pigments. Tetrahydroanthraquinone is used as a catalyst to facilitate the chemical pulping of wood for paper manufacture. This technology has been pioneered in Japan where it is used primarily with Kraft pulping, which employs sodium hydroxide and sodium sulfide to disengage lignin from the wood and leave cellulose fibers. In conventional pulping, the 1,4-glycosidic linkages of cellulose are hydrolyzed and reduce the yield of pulp. Tetrahydroanthraquinone apparently accelerates the extraction of lignin while inhibiting attack on the cellulose. Higher yields of pulp result.

9.8.1 Hydrogen Peroxide

2-Ethylanthraquinone is the catalyst in the autooxidation route for the manufacture of hydrogen peroxide. The amyl derivative is also used. It is reduced by hydrogen on palladium to the hydroquinone, and then reoxidized with air to give hydrogen peroxide and the original anthraquinone.



Ethylanthraquinone

The economics of the process depend heavily on effective recycling of the expensive and extraction solvents, and of the hydrogenation catalyst. A new “high-productivity/high-yield” process, based on an optimized distribution of isomers of 2-amylanthraquinone, has been developed by Solvay (Section 6.2).

A route to hydrogen peroxide, still only at the laboratory stage, involves the combination of hydrogen and oxygen directly. Previous attempts to do this failed because the gold–palladium catalyst (which offered the best prospects) did not stop at hydrogen peroxide but continued further to produce water. The new gold–palladium catalyst is treated with nitric acid. The nitric acid encourages the formation of gold–palladium nanoparticles that disperse more evenly over the surface of the carbon support. This is important because hydrogen peroxide molecules are converted to water at exposed sites on the support. A more even distribution of nanoparticles means fewer exposed sides and a sharp reduction in the formation of water.³²

In 2006, world production of hydrogen peroxide was around 1.9 million metric tons per year and is expected to grow rapidly.

ENDNOTES

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3. Patents describing the Boreskov, Institute of Catalysis’ nitrous oxide based oxidation of benzene to phenol include: WO 95/27560 (12 April 1995) and WO 95/27561 (12 April 1995).
4. Solutia patented a fluidized-bed reactor for nitrous oxide oxidation of benzene to phenol; U.S. Patent 5,892, 132 (6 April 1999).
5. <http://www.chemsystems.com/reports/search/docs/toc/98-3toc.pdf>.
6. The Bayer route to dimethyl carbonate is described in U.S. patents 5,449,9806 (12 September 1995), 5,523,452 (4 June 1996), and 5,334,742 (2 August 1994) all to Bayer. Asahi has a patent that discloses the use of reactive distillation to effect the methanolysis of ethylene carbonate to dimethyl carbonate and ethylene glycol, U.S. Patent 5,847,189 (8 December 1998).
7. U.S. Patent 5,391,692.
8. www.nedo.go.jp/kiban/zairyo/eng/poly/poly005.html.

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10. <http://www.epa.gov/greenchemistry/pubs/pgcc/winners/grcall.html>.
11. *Chem Week*, 31 March 2010.
12. <http://www.senseaboutscience.org.uk/index.php/site/other/515>; P. Walter, *Chem. Ind.* 23 August 2010, p. 7.
13. D. C. MacLaren and M. A. White, *J. Mater. Chem.* **13**, 1695–1700, 2003.
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18. http://www.chemsystems.com/reports/search/docs/abstracts/0405-3_abs.pdf.
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22. For example, N. Hoffmann, E. Löffler, N. A. Breuer, and M. Muhler, On the nature of the active site for the oxidative amination of benzene to aniline over NiO/ZrO₂ as cataloreactant, *Chemsuschem* **1**, 393–396, 2008.
23. World Patent Application 00/09473; *European Chemical News*, 22–28 May 2000, p. 33.
24. Jeroem Vetter, http://beta.wewi.eldoc.ub.rug.nl/FILES/root/2010/asrtm/Rapport_Beta_2010-5.pdf.
25. Limin Liu, Fang Li, Yangji Wang, and Xinqiang Zhao, *Chinese J. Catalysis*, **28**, 667–669, 2007.
26. Yixia Pei, Huiquan Li, Haiao Liu, and Yi Zhang, *Catalysis Today*, **148**, 373–377, 2009.
27. *Chem. Eng. News*, 22 December 2008.
28. The consensus that DDT is wholly bad was debated at the Johannesburg negotiations. Some details are given at www.sciencenews.org/20000701/bob2.asp. A fairly partisan website, www.malaria.org/DDTpage.html, provides an extensive bibliography and www.junkscience.co/ddtfaq.htm questions the evidence that DDT is responsible for the various problems with birds and their eggs. See also a collection of articles at www.malaria.org/DDTpage.html.
29. <http://www.epa.gov/oppsrrdl/REDs/para-dichlorobenzene-red-revised.pdf>.
30. *Chem. Eng. News*, 14 December 1992.
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32. J. Evans, *Chem. Ind.*, 9 March 2009.

CHAPTER 10

Chemicals from Toluene

Toluene is the major product from catalytic reforming (Section 4.8). The chemical industry requires considerably more benzene than toluene, but toluene is preferred for unleaded gasoline because of its low toxicity and high octane number. Catalytic reforming is the major source of toluene in the United States but in Western Europe pyrolysis gasoline is the major source.

Just as propylene has traditionally been cheaper than ethylene, toluene has been cheaper than benzene. Propylene's ready availability and its reactive allylic hydrogens led to the development of a series of brilliant chemical reactions. Attempts to find broad usage for toluene were less successful despite its reactive benzylic hydrogens. These can undergo many of the same chemical reactions as propylene's allylic hydrogens, for example, ammoxidation. Toluene's main nongasoline uses are hydrodealkylation to benzene and disproportionation to benzene and xylenes. These are "swing" operations and occur when the price differential is sufficient. For example, in 2002 they consumed 70% of the toluene isolated from catalytic reforming in the United States.¹

Global production of toluene in 2009 was about 32 million metric tons (see Fig. 9.2) but only about one million metric tons was consumed for chemicals. Much of the remaining 31 million metric tons was subjected to hydrodealkylation and disproportionation (Section 10.1) to augment benzene and xylenes output. Thus toluene's volume is the smallest of the seven basic chemicals. Figure 10.1 shows the end-use pattern. Western Europe and the United States differ markedly. There is surplus gasoline fraction in Western Europe, hence toluene is not added to gasoline and naphtha is available for cracking. Toluene is instead extracted from the pygas stream and converted to benzene.

10.1 HYDRODEALKYLATION, DISPROPORTIONATION, AND TRANSALKYLATION²

In situ hydrodealkylation during catalytic reforming was discussed in Section 4.8 as an additional source of benzene in that reaction. Hydrodealkylation in a dedicated

Industrial Organic Chemicals, Third Edition. By Harold A. Wittcoff, Bryan G. Reuben, and Jeffrey S. Plotkin.

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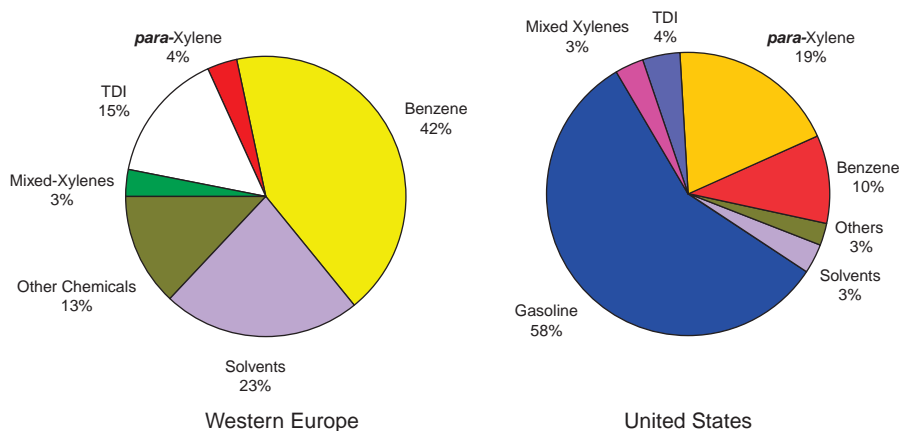
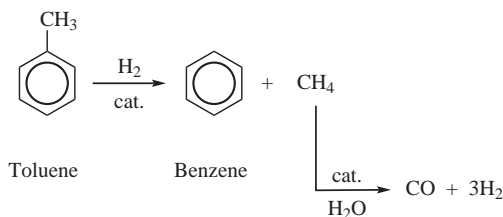


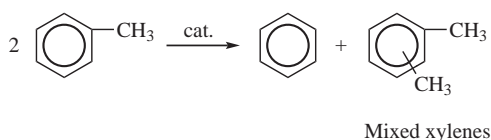
FIGURE 10.1 Toluene end-use pattern (2008). “Others” includes benzoic acid, benzaldehyde, benzyl chloride, and toluenesulfonic acid.

plant may be purely thermal or it may be catalyzed by metals or supported metal oxides. Hydrogen is always present. Typical reaction conditions are 600°C and 40–60 bar over oxides of chromium, platinum, molybdenum, or cobalt supported on alumina. The uncatalyzed reaction requires a higher temperature of up to 800°C and a pressure up to 100 bar.



Methane forms and, in one version of the process, it is subjected to the synthesis gas reaction (Section 12.4) to provide hydrogen for the hydrodealkylation. Despite the cost of catalyst, the catalytic method is preferred because it allows for higher conversion and gives greater selectivity so that 92+% benzene results.

Variants of hydrodealkylation are disproportionation and transalkylation. In disproportionation, two molecules of toluene react to give one of benzene and one of mixed xylenes.

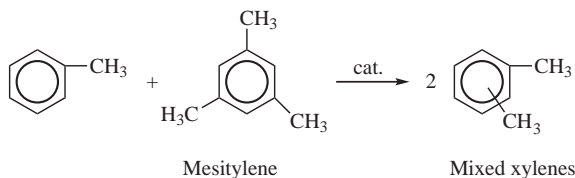


Disproportionation is important as a source of mixed xylenes from which the *para* isomer, the one most in demand, can be isolated. The reaction is carried out in the vapor phase in the presence of a nonnoble metal catalyst. Even a casual estimate of the energetics of the reaction indicates that the equilibrium constant is close to unity, so large volumes of reactants must be recycled from the product-recovery section of the plant to the reactor. The advantage of the process, compared with catalytic reforming, is that the reactor effluent is free from ethylbenzene. This makes the separation of the xylene isomers easier, and crystallization may be used (Chapter 11).

Disproportionation is formally (but not mechanistically) similar to metathesis (Section 4.14). Both produce two more valuable products from one less valuable one. It has assumed major importance in the United States and, in 2009, 900,000 metric tons of benzene was produced by this process.

A dramatic improvement developed by Mobil in the mid to late 1980s was the development of a liquid phase process based on a shape-selective, antimony-doped zeolite ZSM-5 catalyst at 300°C and 45 bar. A xylene fraction results with as much as 95–99% of the desired *p*-xylene. The disproportionation takes place inside a zeolite cage whose “mouth” is shaped such that benzene, toluene, and *p*-xylene have ready access but *ortho*- and *meta*-xylenes cannot escape (Section 18.9). Accordingly, these isomers remain in the cage to undergo further isomerization and to supply the equilibrium quantities required each time 2 moles of toluene disproportionate. These types of process, termed “selective toluene disproportionation,” are now offered by several licensors such as UOP, Axens, and GTC. *para*-Xylene selectivities in the range of 95–99% can now be achieved, but at these high selectivities toluene conversion per pass is reduced to 20–23%.

Transalkylation involves the interaction of toluene with 1,3,5-trimethylbenzene or mesitylene, a compound produced during catalytic reforming.



A methyl group migrates from a trimethylbenzene molecule to a toluene molecule giving two molecules of mixed xylenes. The reaction is carried out in the presence of hydrogen. In practice, benzene is also produced, but its volume can be kept low by use of a high ratio of trimethylbenzene to toluene.

It would be advantageous if toluene could be converted entirely to *p*-xylene, without benzene, and Lummus/SABIC announced in 2010 a project to alkylate toluene with methanol to *p*-xylene. This would be related to Exelus's alkylation of toluene with methanol to give styrene (Section 5.8).³ It involves a catalyst based on phosphorus-modified ZSM-5 zeolites. Previous catalysts for this conversion have deactivated quickly; the new one presumably is longer lived.

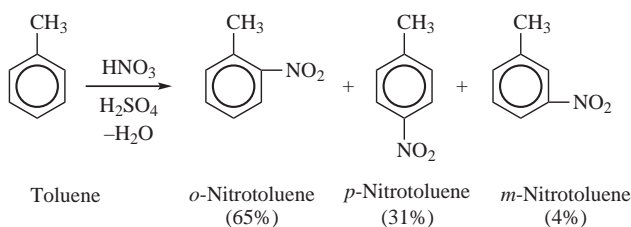
10.2 SOLVENTS

Toluene's main use, apart from its role in gasoline, is as a secondary source of benzene – see above. Its second largest use is as a solvent mainly for coatings. The realization that benzene is carcinogenic has increased toluene's solvent usage at the expense of benzene, although the latter was in any case small. Toluene is a primary solvent for coatings based on medium and short oil alkyd resins (Section 11.1.2) but is a so-called latent solvent for nitrocellulose lacquers, which require as primary solvents polar compounds such as esters, ketones, and glycol ethers.

10.3 DINITROTOLUENE AND TOLUENE DIISOCYANATE

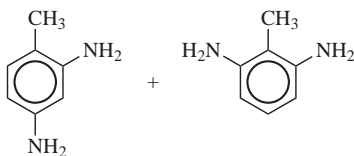
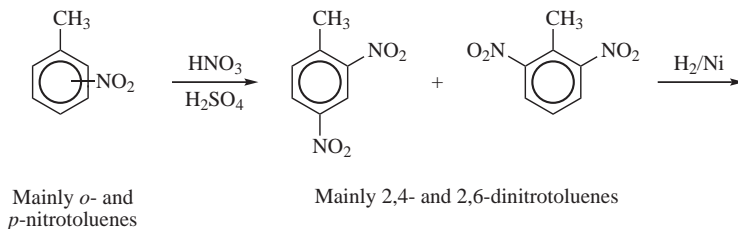
The largest outlet for toluene in which its chemical properties are of value in their own right is as a raw material for a mixture of 2,4- and 2,6-toluene diisocyanate (tolylene diisocyanate, diisocyanatotoluene, TDI) used for polyurethane resins. Global demand is 1.7 million metric tons. Eighty-five percent of TDI goes into flexible foams and 10% into coatings. Commercial TDI contains about 80% of 2,4- (*ortho,para*) isomer and 20% of the 2,6- (*ortho,ortho*) isomer.

TDI is made by chemistry similar to that used for 4,4'-diphenylmethane diisocyanate (MDI) (Section 9.3.1).⁴ The three-step process comprises the dinitration of toluene; the hydrogenation of the nitro compounds to diaminotoluenes; and the reaction of these with phosgene to commercial grade TDI. Toluene is nitrated with a mixture of nitric and sulfuric acids in two stages. The first produces the three isomers of mononitrotoluene.



These are subsequently nitrated further to obtain the six possible dinitrotoluene isomers. The 2,4-isomer comprises 74–76% of the mixture and the 2,6-isomer about 19–21%. The concentrations of the other four isomers are minimal. The 3,4-compound forms at a level of 2.4–2.6%. The 2,3-, 2,5- and 3,5-isomers are present at a level of no more than 1.7%. The concentration of the acids is carefully controlled so that very little of the trinitro isomers forms.

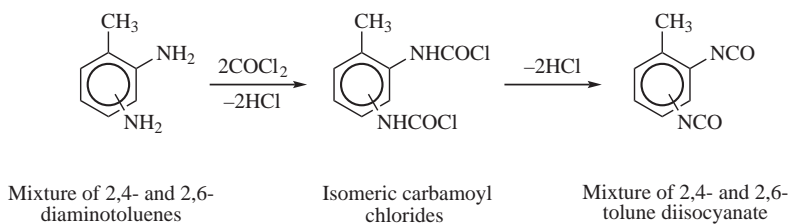
The dinitrotoluenes are dissolved in methanol and hydrogenated continuously to diaminotoluenes by reaction with hydrogen in the presence of Raney nickel at 150–180°C and 65–130 bar. Numerous other catalysts such as supported platinum or palladium may be used.



Mainly 2,4- and 2,6-diaminotoluenes

The possibility of eliminating the nitration step by an intermolecular amination of toluene with ammonia is of some interest. Similar chemistry has been discussed for the possible preparation of aniline (Section 9.3) and *m*-aminophenol (Section 9.7).

The carbonylation with phosgene occurs in two stages, the first yielding a carbamoyl chloride and the second the isocyanate. In both reactions, HCl is liberated. The reaction is carried out with a 12–20% solution of the diamine mixture in chlorobenzene (Section 9.6). This is combined with a chlorobenzene solution of phosgene.



Carbamoyl chloride formation occurs at 0–30°C and isocyanate formation at 160–180°C. Conversion is about 80%. Treatment of the residue with alkali provides unreacted diaminotoluene for recycle.

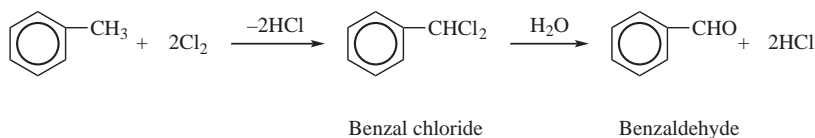
TDI is extremely toxic as is phosgene. Various nonphosgene routes to TDI have been suggested, the most significant of which is EniChem's Urethane Pyrolysis Process.⁵ This is similar to their MDI process. Oxidative carbonylation of methanol is used to produce dimethyl carbonate (DMC). DMC is then reacted with diaminotoluene to give a urethane intermediate that is then cracked at high temperature and low pressure to give TDI. The process has not yet been fully commercialized.

Dinitrotoluene has another use as a gelatinizing and waterproofing agent in explosive compositions. Additional nitration gives trinitrotoluene (TNT), an

explosive formerly used in military and civilian applications but now of importance only to the military. It is safer than picric acid (Section 9.1) because it does not form detonation-sensitive salts with metals and has a lower melting point (80°C) so that it can be conveniently loaded into shells in the molten state. For civilian explosives, such as those used in mining, ammonium nitrate is the preferred material.

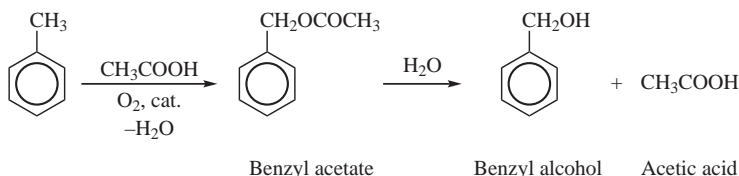
10.4 LESSER VOLUME CHEMICALS FROM TOLUENE

Toluene may be converted to phenol (Section 9.1). It also provides the starting material for one route to caprolactam (Section 9.2.2). In a reaction analogous to the formation of allyl chloride from propylene (Section 6.11.1), the methyl group of toluene can be chlorinated to yield benzyl chloride, which may be used to quaternize tertiary amines such as lauryldimethylamine to give germicidal compounds. Its main use is as a raw material for the minor PVC plasticizer, butyl benzyl phthalate. The presence of the aromatic ring appears to confer stain resistance to poly(vinyl chloride) floor coverings. Dichlorination of the methyl group of toluene leads to benzal chloride, which on hydrolysis provides benzaldehyde, an ingredient of flavors and perfumes. This is the most important route to benzaldehyde, which is also a valuable by-product of the toluene-to-phenol process (Section 9.1).

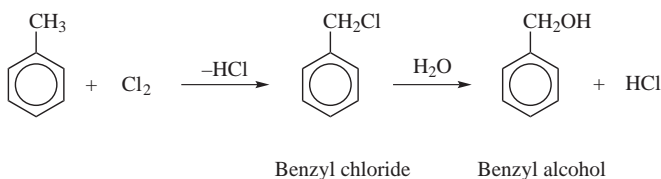


It may also be made by direct oxidation of toluene. This is usually accomplished in the liquid phase with air at about 100°C and 3 bar with cobalt salt catalysts. In another process the oxidation is carried out in acetic acid with cobalt and manganese acetates as catalysts. This is analogous to the process used for the preparation of terephthalic acid (Section 11.3).

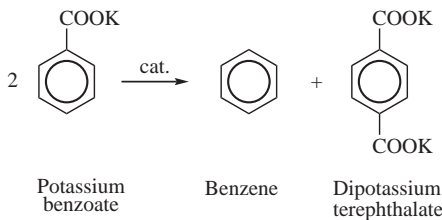
The oxidation of toluene gives not only benzaldehyde but also benzyl alcohol, just as the oxidation of propylene provides acrolein and allyl alcohol (Sections 6.11.1 and 6.11.4), although the mechanisms are different. These normally occur as recyclable by-products during benzoic acid formation. If benzyl alcohol is required by direct oxidation, the reaction is carried out in the presence of acetic acid, which captures the alcohol as benzyl acetate before it is oxidized further to benzoic acid. The same technique is used in the oxidation of propylene to allyl alcohol.



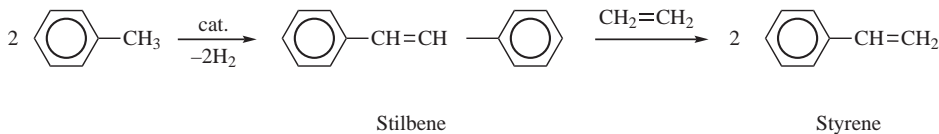
The most important route to benzyl alcohol, however, is by the hydrolysis of benzyl chloride.



Benzoic acid is a halfway state in a minor process for phenol manufacture (Section 9.1), but benzoic acid itself has a few small uses. Diethylene glycol dibenzoate is a useful nonstaining plasticizer for PVC flooring, where it competes with butyl benzyl phthalate. Butyl benzoate is a perfume ingredient. Benzoic acid is an intermediate in a caprolactam synthesis (Section 9.2.2) and in a process for the production of terephthalic acid known as the Henkel II reaction. This involves the disproportionation of potassium benzoate to benzene and the potassium salt of terephthalic acid. It is noteworthy because of the *para*-directiveness of the potassium ion. The process has been used in Japan.

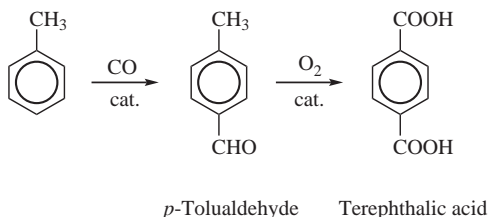


The conversion of toluene to *p*-methylstyrene has already been described (Section 5.8). There is, however, an uncommercialized but chemically interesting process for styrene from toluene. Toluene is dehydrocoupled to stilbene followed by a metathesis reaction with ethylene. The first step takes place at 600°C in the presence of a lead magnesium aluminate catalyst and the second at 500°C with a calcium oxide – tungsten oxide catalyst on silica.



The carbonylation of toluene leads to *p*-tolualdehyde, which can be oxidized to terephthalic acid (Section 11.3.2). The reaction is catalyzed by a combination of HF

and BF_3 to give selectivities of about 97% at 85% conversion. This process has not been commercialized because, despite the use of low cost toluene as feedstock, this process cannot compete economically with the conventional *para*-xylene based route. In addition, the HF/BF_3 catalyst system is corrosive and difficult to handle.



ENDNOTES

1. NexantChemSystems PERP report 02/03-5, *Benzene/Toluene* (April 2003).
2. UOP has issued a series of patents relating to improvements in toluene disproportionation and transalkylation technology: U.S. Patent 6,383,967 (7 May 2002), U.S. Patent 6,359,185 (19 March 2002), U.S. Patent 6,191,331 (20 February 2001), U.S. Patent 6,355,852 (12 March 2002), U.S. Patent 6,008,423 (28 December 1999), U.S. Patent 6,239,056 (29 March 2001), and U.S. 6,063,977 (16 May 2000).
3. <http://www.icis.com/Articles/2011/01/10/9424069/c1-based-advances-boost-feedstocks.html>.
4. Nexant ChemSystems' PERP report 98/99S8, *MDI/TDI*.
5. http://www.chemsystems.com/about/cs/news/items/PERP%200708S9_TDI.cfm.

CHAPTER 11

Chemicals from Xylenes

Xylenes are produced worldwide mainly by catalytic reforming (Section 4.8; see also Fig. 9.2). This is so even in Europe where most of the benzene and about half of the toluene comes from pyrolysis gasoline. The xylenes are isolated only with difficulty from pyrolysis gasoline because it contains about 50% ethylbenzene with a similar vapor pressure. Accordingly, the C₈ fraction of pyrolysis gasoline is usually returned to the gasoline pool.

A comparison of the C₈ fractions from catalytic reforming and pyrolysis gasoline was shown in Figure 4.10 together with the end-use requirements. The chemical industry needs to separate the xylene isomers (*ortho*, *meta*, *para*), isomerize the unwanted ones to an equilibrium mixture, and repeat the process to extinction.

The separation of the three xylene isomers and ethylbenzene from each other is an awesome task.¹ Their physical constants are shown in Table 11.1. The boiling points of all four compounds are within 9°C. *o*-Xylene boils more than 5°C above the others, however, and may be separated by fractional distillation on a huge column with 150–200 plates and a high reflux ratio. The mixture at the top of the column contains about 40% *m*-xylene, 20% *p*-xylene, and 40% ethylbenzene. If required, the low boiling ethylbenzene can be removed by an involved extractive distillation. Energy costs are high and the ethylbenzene is sometime allowed to remain for further processing.

The isomers in the intermediate fraction differ markedly in melting point and, in the older process, they are separated by low temperature crystallization. The mixture is carefully dried to avoid icing of the equipment and then cooled. Crystallization of *p*-xylene starts at –4°C and continues until –68°C, at which point the *p*-xylene/*m*-xylene eutectic starts to separate, so the procedure is halted. The first stage only raises the *p*-xylene concentration in the crystalline mass to 70%, but a series of melting, washing, and recrystallization steps eventually increases this to 99.5%.

If *m*-xylene is required, it may be extracted from the C₈ stream by complex formation. Treatment of the stream with HF·BF₃ gives two layers. The *m*-xylene

TABLE 11.1 Physical Constants of the C₈ Stream

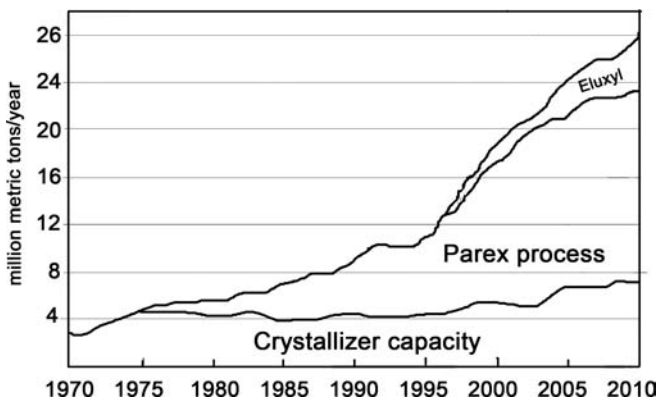
Stream Components	Melting Point (°C)	Boiling Point (°C)
<i>o</i> -Xylene	−25.2	144.4
<i>m</i> -Xylene	−47.9	139.1
<i>p</i> -Xylene	13.2	138.3
Ethylbenzene	−95.0	136.2

selectively dissolves in the HF-BF₃ layer as the complex C₆H₄(CH₃)₂·HBF₄. The phases are separated and the *m*-xylene regenerated by heating.

The drawbacks of the low temperature crystallization are the high energy requirements for cooling and the problems of handling the solid *p*-xylene which, for example, deposits on the walls of the cooling vessel and thus reduces the rate of heat transfer. Nonetheless, it is still used particularly if *p*-xylene content is high, as it is if produced by disproportionation (Section 10.1).

The more recent processes for separating the *m*- and *p*-xylenes make use of molecular sieves for which the feed components show small differences in affinity. The UOP Parex process started in 1971. A newer related process, called Eluxyl, has been pioneered by Chevron and Axens (formerly IFP).^{2,3} Figure 11.1 indicates that they account for almost all the new capacity installed since then. These two processes are analogous to the one used to separate linear and branched chain hydrocarbons (Section 9.4). They are based on a continuous countercurrent flow of liquid and solid adsorbent. This is achieved in a novel way. The solid bed of adsorbent cannot easily be moved countercurrent to the liquid flow. Instead, countercurrent flow is simulated with a stationary bed of adsorbent by periodically displacing the positions at which the process streams enter and leave the bed. That is, the positions of the liquid feed and withdrawal points are shifted in the same direction as the fluid flow down the bed.

Alternatively, if *m*-xylene is targeted for separation, it can be selectively absorbed from the C₈ stream by passing it through an isothermal bed of solid adsorbent. In UOP's MX Sorbex process,⁴ countercurrent contact of the fluid and solid adsorbent is simulated using the same methodology described for the Parex process above.

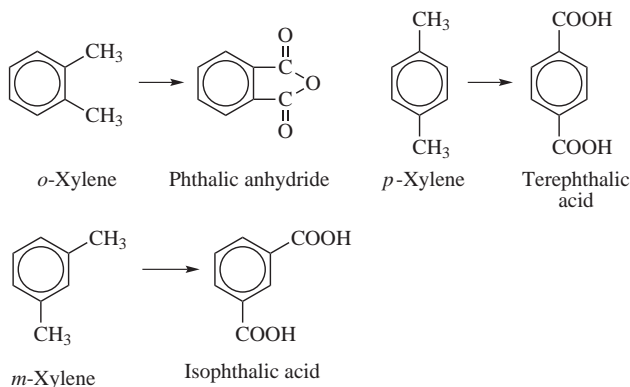
**FIGURE 11.1** World capacity for xylene separations (based on UOP, Axens, and Nexant data).

The exit streams from both the low temperature crystallization and the adsorption processes contain unwanted products. In a *p*-xylene plant, these are primarily *m*-xylene, ethylbenzene (if it was not removed earlier), and the portion of *o*-xylene that the market does not require. They are catalytically isomerized in the presence of acid catalysts to provide another equilibrium mixture, which is somewhat more favorable in that it contains about 48% *m*-xylene, 22% each of *o*- and *p*-xylenes, and 8% ethylbenzene. Acidic catalysts include silica-alumina, and silica with HF-BF_3 , the same material that complexes with *m*-xylene. The drawback of silica-alumina is that it promotes disproportionation and transalkylation. If platinized alumina is added to the silica-alumina, as in a dual function catalyst, the system will isomerize ethylbenzene as well as the xylenes.

The most important isomerization catalyst today is the zeolite ZSM-5. This is the same zeolite catalyst useful for toluene disproportionation to benzene and *p*-xylene (Section 10.1). The silica-alumina/platinized-alumina catalyst operates at 23–33 bar in a hydrogen atmosphere with substantial recycle. ZSM-5 has a major economic advantage because it operates at low pressures either in the vapor or liquid phase and requires less or even no hydrogen and much less recycle than does the noble metal catalyst. Its one disadvantage is that it does not isomerize ethylbenzene but rather dealkylates it to benzene. Because the ZSM-5 process requires less capital investment and provides lower operating costs, it has been widely accepted. A process announced but not commercialized makes use of nonzeolite molecular sieves, primarily silicoaluminophosphates. This process is claimed not only to isomerize ethylbenzene to xylenes but also to provide a higher level of the desired *p*-xylene.

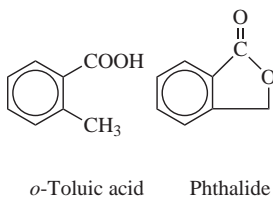
Several unconventional processes for producing aromatics were commercialized in the late 1990s. They catalytically converted low-valued materials such as LPG, light olefins, and C_6 and C_7 alkanes to aromatics. Examples include BP/UOP's Cyclar process, Chevron's Aromax process, and Asahi's Alpha process. Xylenes are typically the smallest fraction of aromatics from these processes.

Mixed xylenes are used as solvents, particularly in the paint industry, and are valued components of the gasoline pool because of their high octane number. The major chemical use for the individual xylenes is oxidation of *p*-xylene to terephthalic acid, *m*-xylene to isophthalic acid, and *o*-xylene to phthalic anhydride.

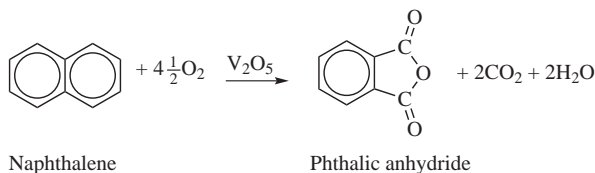


11.1 *o*-XYLENE AND PHTHALIC ANHYDRIDE

o-Xylene may be oxidized to phthalic anhydride in gas or liquid phase processes and in fixed or fluidized beds. The liquid phase oxidation makes use of metal salt catalysts that are soluble in the reaction medium. The gas phase fluidized bed process takes place at 375–410°C over a classical vanadium pentoxide catalyst. The process is highly exothermic, and the fluidized bed offers better temperature control and less risk of explosion. It also enables the handling of phthalic anhydride as a liquid (melting point 130.8°C). Yields were initially rather low, probably less than 80%, but have improved over the past decade. There were also side reactions leading to *o*-toluic acid, phthalide, benzoic acid, and maleic anhydride as well as to the complete oxidation to carbon dioxide and water.



As a result of the low yields, an older route to phthalic anhydride, based on coal tar naphthalene (Section 14.1) has remained viable. The oxidation is similar, again with a vanadium pentoxide catalyst. Indeed, some plants can operate with either feedstock. The reaction is analogous to the oxidation of benzene to maleic anhydride (Section 7.4.2).



In the United States all production is now from *o*-xylene with only Koppers having the facility to switch feedstocks. Sixteen percent of global phthalic anhydride production is based on naphthalene.⁵

The *o*-xylene process is somewhat less exothermic (1108 kJ/mol as against 1794 kJ/mol) because there are fewer carbon atoms to be oxidized. The loss of two carbon atoms from naphthalene as carbon dioxide is an economic drawback of the process, which is balanced by the higher yields.

Naphthalene is available from the distillate from coke ovens and is one of the few coal tar chemicals still of importance. It is also made by the hydrodealkylation of the methylnaphthalenes produced by the catalytic reforming of gas oil fractions. Only about 2.0% of U.S. phthalic anhydride comes from naphthalene. The proportion is higher in Europe.

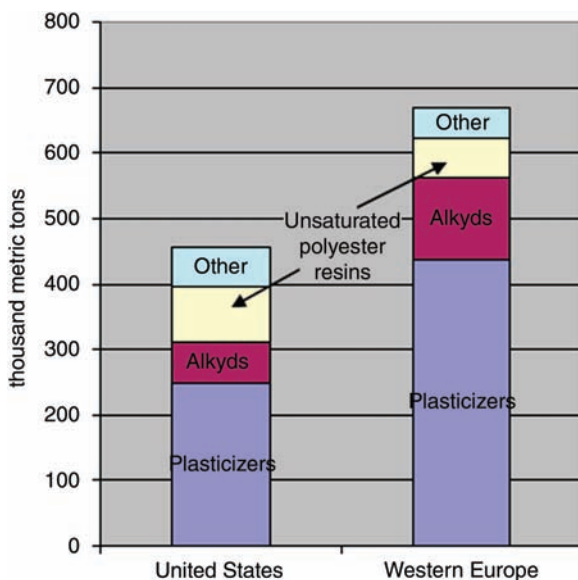
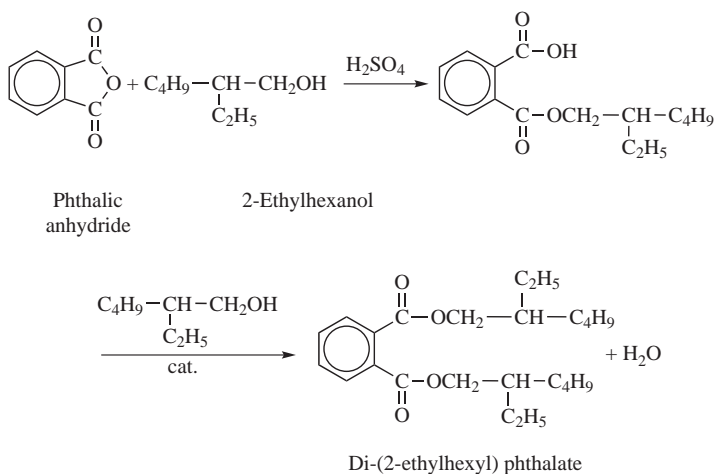


FIGURE 11.2 Phthalic anhydride end-use pattern (2009).

11.1.1 Plasticizers

About 60% of phthalic anhydride production was used for plasticizers in 2008 (Fig. 11.2). About 17% goes into alkyd resins and most of the remainder into unsaturated polyester resins (see below). All three of these applications involve esterification of phthalic anhydride and are mature. As with all anhydrides, the esterification proceeds in two stages. The first, shown below with 2-ethylhexanol, the most important plasticizer alcohol, goes readily to form the half ester, whereas the second step proceeds only with the aid of a catalyst such as *p*-toluenesulfonic acid and a temperature of 160°C.



At a temperature between 185°C and 205°C, a noncatalytic esterification takes place, obviating the catalyst removal steps. With both routes color development must be avoided. The plasticizer has a high boiling point and, once formed, is difficult and expensive to distill or otherwise purify.

The manufacture of plasticizers is the largest outlet for phthalic anhydride, so this is an appropriate place for a digression on them. A plasticizer is a material that is compatible with a polymer resin and softens it or decreases its brittleness. If 50 parts of di-(2-ethylhexyl) phthalate are milled with 100 parts of poly(vinyl chloride), for example, a soft pliable material is obtained. Variation of the amount of plasticizer permits the achievement of any desired degree of softness. The plasticizer also makes the resin easier to process.

Plasticizers are not universally applicable, however, because there are many polymers with which no known plasticizers are compatible. Compatibility is governed by complex interactions including hydrogen bonding, dipoles, Van der Waals forces, cohesive energy density, and solubility parameter. These factors also govern miscibility in liquid – liquid systems, and the plasticizer compound may be thought of as a solution of plasticizer in polymer. Most resins undergo sudden transition from a rigid solid to a soft gel as the plasticizer content is increased above a critical value, or as the temperature is increased. Consequently, only a few polymers can usefully be plasticized. Examples include cellulose esters, poly(vinyl acetate), some synthetic rubbers, a few phenolic and amino resins, and amide and protein polymers. In general, esters seem to be the most suitable materials. Service requirements for plasticizers are shown in Table 11.2.

About 90% of all plasticizers are used with PVC. It is unique in its acceptance of large amounts of plasticizer with controllable change in physical properties. Di-(2-ethylhexyl) phthalate (DEHP) is the most widely used PVC plasticizer. Other phthalates of commercial importance are dibutyl phthalate (DBP), di-*n*-octyl phthalate (DNOP), di-isononyl phthalate (DINP), di-isodecyl phthalate (DIDP), and butylbenzyl phthalate (BBzP). BBzP is commonly used as a plasticizer for vinyl

TABLE 11.2 Service Requirements for Plasticizers

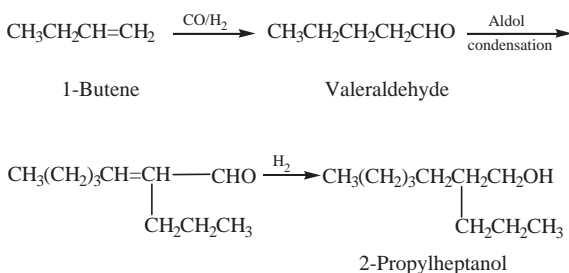
Plasticizer properties

- Compatibility with resin
- Softening power
- Stability to light and to processing temperatures
- Gelation temperature (the temperature at which the plasticizer begins to fuse with the resin)
- Price

Properties of plasticized compound

- Mechanical properties of plasticized polymer (called the “compound”)
 - Volatile loss at room temperature and (if necessary) on heating
 - Extractibility by water, detergent solutions, and organic solvents
 - Low temperature properties (retention of flexibility on cooling)
 - Electrical properties (volume resistivity, dielectric loss)
 - Fire and toxic hazard
 - Volume cost
-

foams, which are often used as floor tiles and in traffic cones, food conveyor belts, and artificial leather. DINP and DIDP are used when a degree of high temperature resistance is required. Perstorp is building a plant in Sweden, to come onstream in 2014, to make a high temperature plasticizer di-(2-propylheptyl) phthalate.⁶ 2-Propylheptanol will be made by hydroformylation of 1-butene to valeraldehyde followed by an aldol condensation of the valeraldehyde to give a decenal, which can be hydrogenated to 2-propylheptanol.



The U.S. market for phthalate plasticizers in 2008 was about 363,000 metric tons. The proportions of plasticizer added to PVC ranges from 5% to 50%, depending on the degree of softness required, but 30 parts plasticizer to 100 parts resin is typical. At one time DEHP was used to make PVC leathercloth for automobile upholstery, but on hot days it sublimed onto the inside of windshields, giving a very thin but exceptionally greasy layer that fogged the windshield. Straight chain alcohols give plasticizers with lower volatility and better softening power but are more expensive.

Not all plasticizers, even for PVC, are phthalates. Dialkyl adipates and sebacates have better low temperature properties. The trioctyl ester of trimellitic anhydride (Section 12.6) is a low volatility plasticizer that can be used at higher temperatures. Epoxidized oils (usually soybean) plasticize as well as stabilizing PVC. There is also a large group of so-called polymeric plasticizers that are polyesters with molecular weights between 1000 and 7000, much lower than those of polyester fibers. These are made from dibasic acids [general formula $\text{HOOC}(\text{CH}_2)_n\text{COOH}$; adipic: $n = 4$, azelaic: $n = 7$, sebacic: $n = 8$] and a dihydric alcohol (propylene or ethylene glycol). The chain length is controlled ("stopped") by addition of a monofunctional acid or alcohol (e.g., lauric acid or butanol). Polymerics have the best resistance to extraction by solvents and the lowest volatile loss. On the other hand, they have lower softening power than monomeric plasticizers.

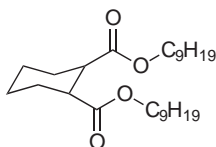
Notable exceptions to the generalization that plasticizers are long chain dialkyl phthalates include tributyl phosphate, which is used as a plasticizer for cellulose esters such as cellulose nitrate and acetate, and tricresyl phosphate, which not only plasticizes cellulose but also acrylate lacquers, PVC, and some rubbers. Phosphates additionally act as a fire retardants. Cellulose nitrate may also be plasticized with camphor, and cellulose acetate with diethyl or dimethyl phthalate or amyl phosphate. Tributyl citrate is used as a solvent and plasticizer for polymers, especially for PVC and its copolymers, if they are subsequently to be applied to food wrapping film. It is permitted in the field of food additives, food contact materials, and medical and pharmaceutical applications.

Because they are not part of the polymer in which they are incorporated and might migrate into food or evaporate into the atmosphere, phthalates are seen as presenting an environmental hazard. When fed in very high doses to mice, they can cause changes in hormone levels, birth defects, liver damage, and other metabolic disorders. On the other hand, plasticized PVC has widespread medical applications, especially for blood bags, because the bags can be sterilized at 120°C. Furthermore, DEHP appears to be beneficial to the production of cholesterol and phospholipid production during storage of blood. A dose-response curve showed that the greater the concentration of DEHP to which the red blood cells were exposed, the lower the hemolysis (death of red blood cells) during storage.⁷

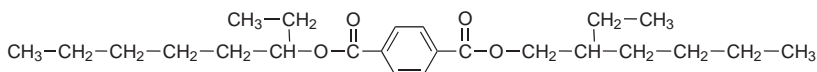
Thus attacks on the medical applications of phthalates have not succeeded, but the European Union has broadly similar legislation banning DEHP, DBP, and BBP from all products for children from any age and DINP, DIDP, and DNOP from toys for children aged under three that might be sucked.⁸ The situation is remarkably well documented by Wikipedia.⁹

To conform to the legislation, BASF has switched from 2-ethylhexanol to 2-propylheptanol (see above) to make a plasticizer called di-isononyl-cyclohexane dicarboxylate (DINCH) for use in sensitive applications. DINCH has been approved by the European Food Safety Authority for use in food contact applications such as cling film, tubes, and sealants.

Another nonphthalate plasticizer, this one produced by Dow, is di-(2-ethylhexyl) terephthalate (Eastman 168).¹⁰ Although isomeric with DEHP, it does not metabolize in the same way. DEHP metabolizes giving the monoester, which may well cause the toxicity problems, whereas Eastman 168 goes directly to terephthalic acid, which is readily metabolized further.

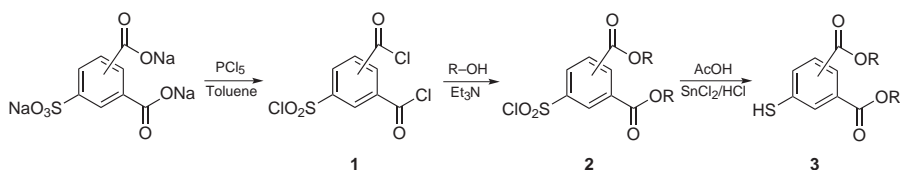


Di-isononyl-cyclohexane dicarboxylate (DINCH)



Eastman 168, di-(2-ethylhexyl) terephthalate

Another solution to the phthalate extraction problem is for it to be bound into the polymer chain. A Spanish group¹¹ has recently produced a DEHP molecule with a thiol group in the 4-position:



This plasticizer (structure **3**) can be based on isophthalic acid as well as phthalic acid. It bonds with PVC via its thiol group and hence becomes an internal plasticizer (see below) and neither extracts nor migrates. The drawback is likely to be the additional expense of producing the mercapto derivative.

Internal plasticizers, apart from the mercapto derivative above, are monomers that are polymerized with vinyl chloride, or some other monomer to give a copolymer of softness intermediate between those of the two homopolymers. An example of an internal plasticizer is 2-ethylhexyl acrylate, which plasticizes vinyl acetate in a water-based emulsion paint. The poly(vinyl acetate) film is otherwise too brittle. Vinyl chloride internally plasticized with 10% vinyl acetate was formerly used for the traditional vinyl phonograph records. The question arises as to why internal plasticizers are not always used, and the answer lies with the convenience of the fabricator, who can add varying amounts of plasticizer to an unplasticized PVC to achieve a desired softness, rather than stocking a whole range of copolymers.

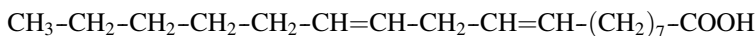
A final group of plasticizers is the epoxidized oils, and they also act as stabilizers for PVC. They are discussed in Section 15.9.

11.1.2 Alkyd Resins

Alkyd resins are oligomers in which polyester functions have been inserted into natural oils such as linseed or soybean. Air-drying alkyds were developed in the early 1930s. Before that, gloss paints were based on drying oils themselves. Drying oils are triglycerides containing unsaturated fatty acid residues (Section 15.3). About 50% of the fatty acid in linseed oil is linolenic acid:



while linoleic acid has one fewer double bonds:

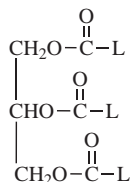


It comprises about 50% of the fatty acids in soybean oil which, because less unsaturation is present, is called a semidrying oil.

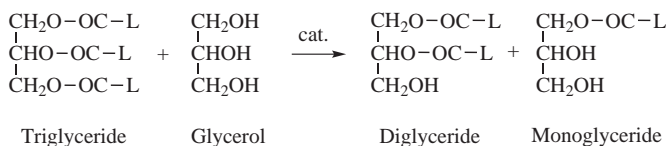
The drying oil, primarily linseed oil or tung oil, was dissolved in a solvent and mixed with pigment. An oil-soluble metal salt such as lead or cobalt naphthenate was added as an initiator. It induced peroxide formation when the paint was spread as a thin film. The peroxide in turn catalyzed the polymerization of the double bonds in the linseed or tung oil to a crosslinked paint film. Soybean oil was unsuitable because it does not contain enough unsaturation to achieve adequate crosslinking. It is valuable in alkyds (see below) because the alkyd has six to ten fatty acid residues, whereas the oil has only three. In other words, the alkyd has greater functionality.

The oil-based paints had little resistance to solvents, chemicals, or ultraviolet light. They were largely replaced by oil-modified alkyd resins, which are made by heating or interesterifying a drying oil with a polyol such as glycerol and esterifying the

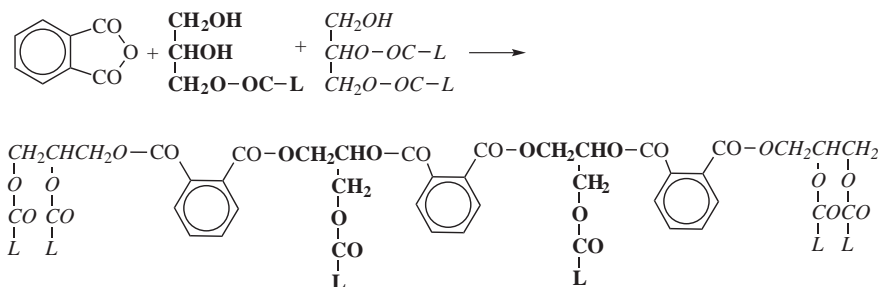
mono- and diglycerides produced with a dibasic acid or anhydride such as phthalic anhydride. If linoleic or linolenic acid is written L-COOH then the triglyceride is



Interesterification with glycerol gives a mixture of esters:



These react with phthalic anhydride to give a more or less linear polymer, the chain length of which is determined by the ratio of mono- to diglycerides in the mixture, the latter acting as chain stoppers. (Monoglyceride units are shown in **bold**; diglyceride units in *italic*.) This polymer is called an alkyd.



The incorporation of the polyester function gives the paint film greater solvent and UV resistance and also imparts somewhat greater corrosion resistance.

Most alkyd resins are made either from soybean oil, which is rich in a mixture of oleic and linoleic acids, or from tall oil acids (Section 15.3), which are also mixtures of these acids. Over 400 different alkyds are available commercially, varying in the type and amount of fatty acid present. Also, instead of the glycerol nature provides in fats and oils, the more highly functional synthetic pentaerythritol (Section 5.11.3) may be used. Maleic anhydride or occasionally other dibasic acids can be included. In another variation, part or all of the phthalic anhydride can be replaced by toluene diisocyanate (Section 10.3) to impart solvent and chemical-resistant urethane linkages.

Alkyd paints make up 40% of the U.S. coatings market, compared with 42% of water-based paints and the remainder are powder coatings, 100% solids coatings,

radiation-cured coatings, and E-coatings (electrocoating, electropainting, or electrophoresis lacquering). Solvent-based coatings in 2008 accounted for 1.5 million metric tons of solvents, 45% of them being aromatics such as toluene and xylenes or aliphatics such as hexane and decane. Alkyds make up 27% of the resins for solvent-based coatings (245,000 metric tons). Alkyds are generally applied to outdoor structures, so the volatile organic compounds (VOCs) cannot readily be recovered and evaporate into the atmosphere as the paint dries. This is an environmental hazard and it is added to the fact that alkyd paints depend on petrochemical phthalic anhydride and solvents. Thus alkyds have been losing market share. Low VOC alkyds exist but have inferior performance, as is also the case with water-based acrylics and expensive “permitted” organic solvents such as *t*-butyl acetate. They take too long to dry and have low gloss and decreased corrosion resistance.

11.1.3 Unsaturated Polyester Resin

This problem has been tackled by Sherwin-Williams, which has started to market a novel, low-VOC, water-based acrylic alkyd surface coating that involves a low-VOC, alkyd–acrylic dispersion (LAAD).¹² This polymer dispersion has poly(ethylene terephthalate) segments for rigidity, hardness, and hydrolytic resistance; it has acrylic functionality for improved dry times and durability; and it has soya functionality (from soybean oil) to promote film formation, gloss, flexibility, and cure. As a bonus, the poly(ethylene terephthalate) can come from recycled soft drink bottles. Since the introduction of LAADs in 2010, Sherwin-Williams claims to have eliminated the use of over 800,000 pounds of VOC solvents and other petroleum-based feedstocks.

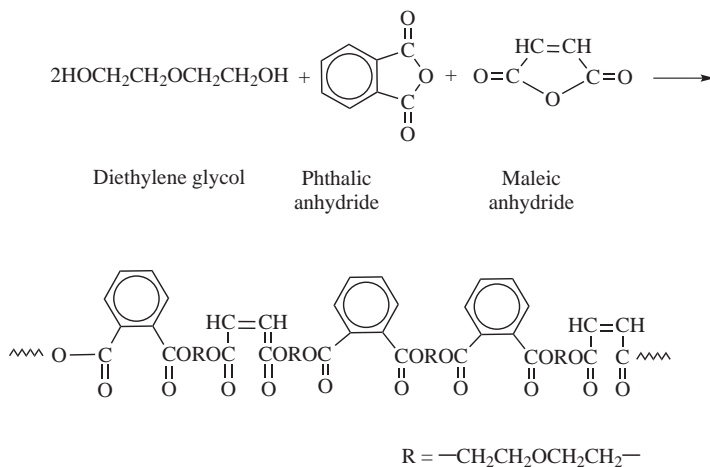
Proctor & Gamble and Cook Composites and Polymers Company have also worked on the above problem and have developed an alternative type of resin related to their failed low calorie fat, Olestra (Section 15.14). They have reformulated their alkyd paints to replace much of the organic solvents by sucrose esters, which themselves are made from renewable sources.¹³

The process starts with fatty acid methyl esters (FAME, Section 15.12.3). The number of double bonds in the mixture is controlled by choice of esters and, if necessary, by hydrogenation. This governs the drying time of the eventual alkyd. The fatty acids are distilled and reacted with sucrose at 275°C to give partial esters, with each sucrose molecule containing between one and four fatty acid residues (see Fig. 15.7). Sucrose is insoluble in fatty acid methyl esters, consequently an emulsifier – potassium stearate – is added, together with a potassium carbonate catalyst. A second reaction stage inserts additional fatty acid residues to give mainly the octa-ester, known as Sefose®. The ester then becomes an involatile modifier of traditional alkyd resins and can be combined with a relatively smaller quantity of conventional alkyds to give Chempol® MPS.

The sucrose ester is claimed to work synergistically with alkyd resins and to crosslink with other constituents in the paint film. Thus it becomes an integral part of the coating film and avoids the VOC problems with conventional solvents.

Unsaturated polyester resins are oligomers that result from the condensation of phthalic anhydride, maleic anhydride, and a glycol such as diethylene glycol.

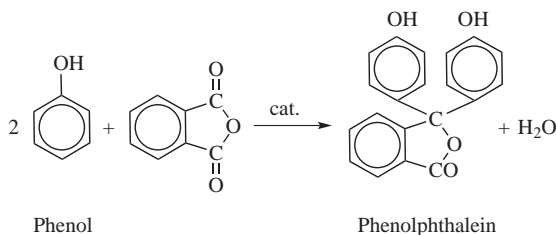
The unsaturated oligomers are copolymerized with styrene or less frequently with methyl methacrylate in the presence of a peroxide initiator. Isophthalic acid may be used to replace part or all of the phthalic anhydride (see below).



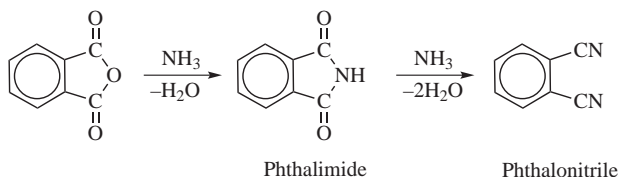
Unsaturated polyester reinforced with glass cloth or fiber was used for the classic automobile, the Corvette. It replaces metal in the fabrication of pipe and storage tanks, and in the manufacture of small boats, and even large minesweepers, where the absence of metal is essential. The fabrication, however, must be done largely by hand (the lay-up and spray-up technique), which introduces an expensive labor component. Some of the hand labor can be eliminated by the use of a process called sheet molding, which makes use of impregnated glass cloth and an initiator that does not become effective until the assembly is heated beyond a threshold temperature. Nonetheless, the technique is primarily of value for short runs of products.

Polyester consumption peaked in 1988 and declined until 1993. Increased automobile usage increased consumption in 1994/1995 and restructuring reduced the number of significant producers from ten to six, but the decline subsequently resumed. The 2008 global market was about 1.4 million metric tons and the U.S. market about 800,000 metric tons.

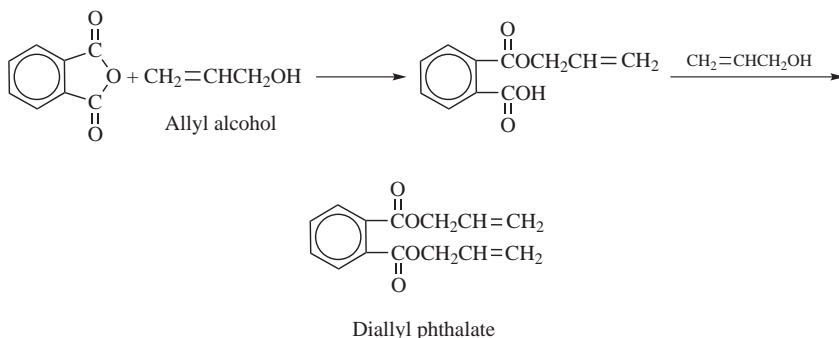
Among the lesser volume uses for phthalic anhydride is its reaction with benzene to form an intermediate which, on dehydration, leads to anthraquinone (Section 9.8). Phthalic anhydride reacts with phenol in the presence of sulfuric acid to form the pH indicator, phenolphthalein.



On reaction with ammonia, phthalic anhydride gives phthalimide which, on further heating with ammonia, dehydrates to give phthalonitrile, the starting material for phthalocyanine dyes.



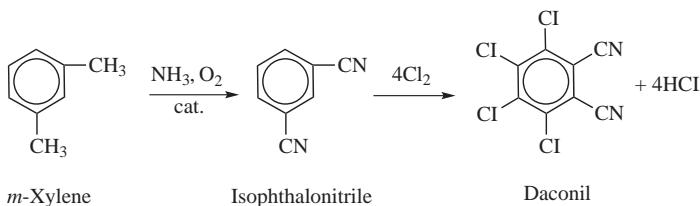
Esterification with allyl alcohol gives diallyl phthalate, a monomer for high performance thermoset polymers, useful for glass-reinforced plastics. The esterification takes place in two steps as with di-2-ethylhexyl phthalate (Section 11.1.1).



A high performance poly(ether imide) “Ultem,” developed by General Electric, involves the condensation of *m*-phenylenediamine with an *o*-phthalic-based dianhydride related to bisphenol A (Section 9.1.2.3).

11.2 *m*-XYLENE AND ISOPHTHALIC ACID

m-Xylene undergoes ammoxidation (Section 6.5) to yield isophthalonitrile, which, on chlorination of the ring positions, gives the fungicide Daconil.

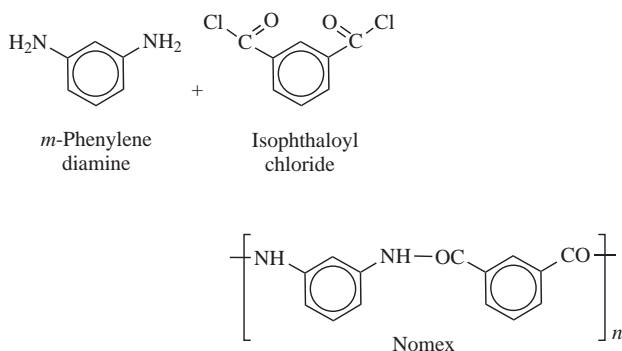


Hydrogenation of the nitrile provides *m*-xylylenediamine, a curing agent for epoxy resins.

Isophthalic acid is made by the oxidation of *m*-xylene by the Amoco – Mid Century process (Section 11.3.1). The highly exothermic reaction takes place at about 200°C and 12 bar with a yield of 95 mol %. Excess oxygen is used.

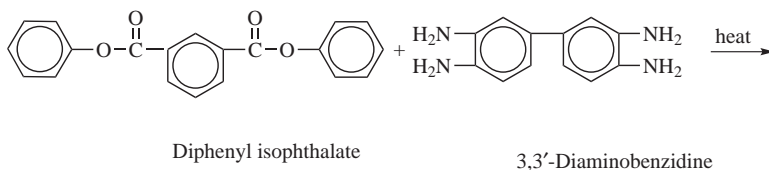
11.2.1 Uses of Isophthalic Acid

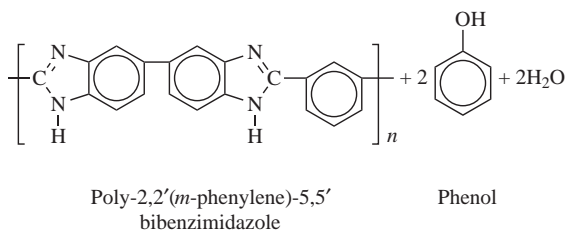
Isophthalic acid has a number of low volume uses. A major one is in unsaturated polyesters, where the greater stability to alkali of the ester linkages enhances the corrosion resistance of the final product. To a lesser extent, it is used in alkyd resins. It goes into specialty plasticizers and its acid chloride, isophthaloyl chloride, is condensed with *m*-phenylenediamine to give Nomex, a high-temperature-resistant nylon, termed an aramid (aromatic polyamide) polymer, useful for fire-resistant cloth for firefighter's and race car drivers' uniforms and more recently for plant workers' clothing.



A growing application for isophthalic acid is as a modifier for poly(ethylene terephthalate) for use in carbonated soft-drink bottle resin. Isophthalic acid, when used to replace a few percent of the terephthalic acid in polyester formulations, serves to disrupt the crystallization of the molten resin as it cools. This feature gives resins that can be processed at lower temperatures saving energy and processing time, and reducing formation of acetaldehyde (a heat degradation product). Isophthalic acid-containing copolyesters also have improved gas barrier properties, an important feature for carbonated beverage bottles (see below). Because crystallization has been reduced, the bottles are more transparent.

Polybenzimidazoles are high-temperature-resistant resins made from the diphenyl ester of isophthalic acid and a tetramine such as 3,3'-diaminobenzidine (3,3',4,4'-tetraaminobiphenyl). They find use as adhesives and laminants for the aerospace industry. Honeycomb bonding provides an example.





11.3 *p*-XYLENE AND TEREPHTHALIC ACID/DIMETHYL TEREPHTHALATE

The major use for *p*-xylene is oxidation to terephthalic acid which, as such or less often as its methyl ester, is reacted with ethylene glycol to give polyester resins for fibers, films, molding resins, and biaxially oriented bottle resins. Terephthalic acid/dimethyl terephthalate is the most widely used xylene-based chemical by a wide margin. In 2008, 35 million metric tons of xylenes were produced globally, of which 93% was the *para*-isomer (32.5 million metric tons), 5% *meta*, and only 2% *ortho*. The 2009 data (in which 27.3 million metric tons was produced) show that 94% of the *para*-isomer was converted to terephthalic acid and 5% to dimethyl terephthalate. Thus about 87% of total xylenes production went into terephthalic acid. The *p*-xylene industry, as with so many branches of the chemical industry, has been migrating to Asia-Pacific. Figure 11.3 shows the expansion of capacity there, compared with the flat data from elsewhere.

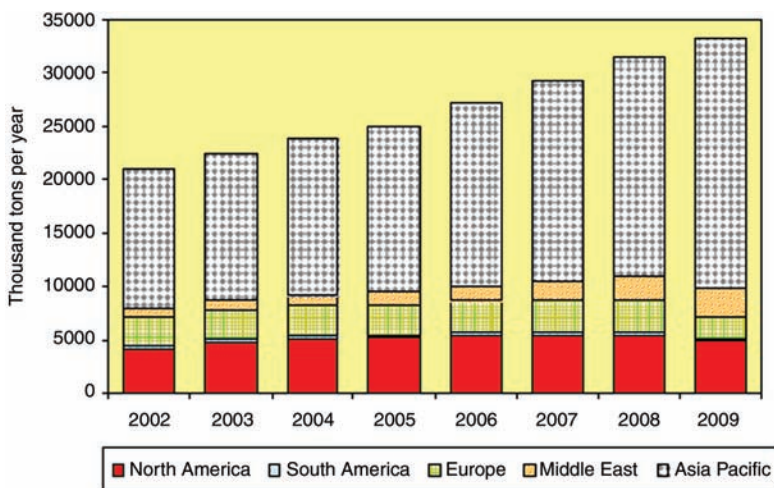
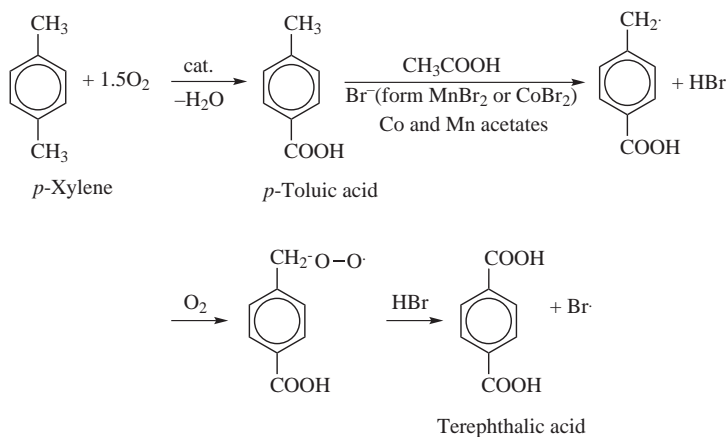


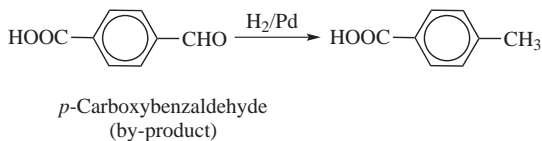
FIGURE 11.3 Regional *p*-xylene capacity.

11.3.1 Oxidation of *p*-Xylene¹⁴

Although *o*-xylene oxidizes readily, *m*- and *p*-xylenes present a problem. The *m*- and *p*-toluic acids formed in the first stage of oxidation contain a methyl group that defies further oxidation, because the carboxyl group is electron withdrawing. There are several ways to overcome this, the most important being the Mid-Century Process developed jointly by Amoco and Scientific Design. The oxidation is carried out in acetic acid solution with a catalyst comprising a manganese or cobalt salt with a bromine promoter, which may actually be bromine itself but is usually manganous or cobaltous bromide. The bromide converts the recalcitrant methyl group to a free radical, which is then much more susceptible to oxidation.



Acetic acid is used as a solvent because terephthalic acid (TPA) is much less soluble in it than are the intermediate products, and this allows for the separation of relatively pure TPA. Much of the acetic acid is oxidized and must be replaced. This is now a growth area for acetic acid (Section 12.5.2.2). Even in its presence, impurities are formed in the reaction, the most important of which is *p*-carboxybenzaldehyde. Crude terephthalic acid containing parts per million of this impurity in aqueous solution is subjected to hydrogenolysis with a palladium catalyst at about 250°C and 36 bar. The impurity is converted to *p*-toluic acid, which, in turn, is separated from the terephthalic acid by fractional crystallization.

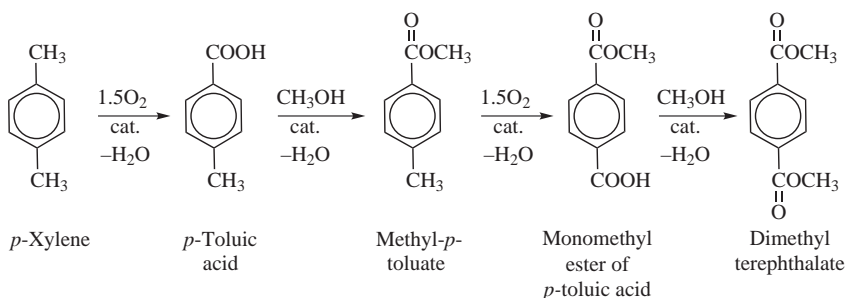


This hydrogenolysis provides the most important industrial use for palladium catalysts. It is this step that made possible the production of sufficiently pure

terephthalic acid to be used directly in the esterification reaction to produce polyester fibers and resins. The purified acid is called PTA (purified terephthalic acid).

Although the mechanism that causes the cobalt bromide to function as a cocatalyst is not completely understood, it has been suggested that the aromatic molecule becomes a free radical because of electron extraction by the cobalt cation. The free radical expels a proton and interacts with oxygen to form a peroxy radical, which then maintains the chain reaction by hydrogen abstraction. Reaction chains are probably very short and the bromide is present to produce oxygen-containing radicals at an optimum rate.

Prior to the development of this process for pure terephthalic acid, it was necessary to use dimethyl terephthalate, which can be purified by distillation, for polyester formation. In early processes, nitric acid oxidized *p*-xylene to crude terephthalic acid, which was then converted for purification to the methyl ester. In another process, *p*-xylene was oxidized to toluic acid, which was esterified to give methyl toluate. The oxidation of the second methyl group is then possible, and the second carboxyl group may then be esterified to give dimethyl terephthalate.



Currently, all new facilities produce purified terephthalic acid rather than the ester, and the latter is being phased out. In 2009, 94% of global capacity produced terephthalic acid. There has been burgeoning growth of polyester fiber production in Asia-Pacific in the late 1980s that will probably continue into the year 2020. Purified terephthalic acid capacity there rose from zero in 1976 to 5000 metric tons/year in 1990 and 36,000 metric tons/year in 2009.

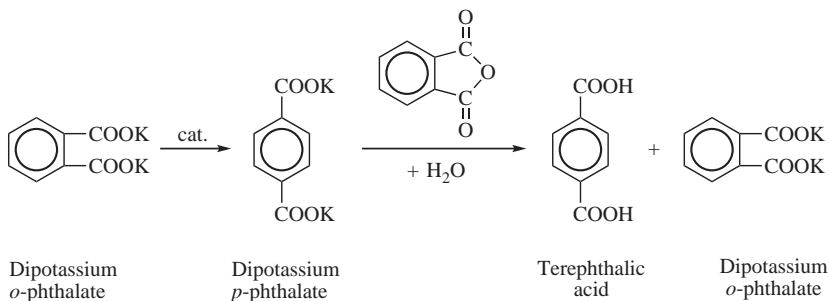
Emphasis on recycling of plastics has made discarded polyester bottles a source of scrap.¹⁵ Polyester bottles can be recycled simply by chopping them up and melting and reprocessing the chips, and this is the commonest method. Carpet fiber is the big use for recycled poly(ethylene terephthalate) in the United States. Nonetheless, polyester scrap is also a source of dimethyl terephthalate and related polyester oligomers. Two main processes are available. In the first, poly(ethylene terephthalate) scrap is treated with methanol to generate dimethyl terephthalate and ethylene glycol, which may be purified by distillation. The second process achieves only a partial depolymerization. A small amount of ethylene glycol is added to the scrap to give a low viscosity oligomer, which is purified by adsorption and filtration. It is then repolymerized under partial vacuum, which removes volatile contaminants and the

ethylene glycol formed during the reaction. Costs of collecting, sorting, and cleaning scrap are a major part of the recycling cost, but it appears that the overall process is similar in cost to the conventional process starting with virgin material. Plastics recycling has been most successful with polyesters. Germany is said to have a returnable bottle policy, in which consumers pay a small deposit on a bottle, which is returned when the bottle is brought back.

11.3.2 Alternate Sources for Terephthalic Acid

There are various other sources for terephthalic acid. The disproportionation of toluene to *p*-xylene, which in turn may be oxidized to terephthalic acid, has been described in Section 10.1 as was the carbonylation of toluene in Section 10.4, and the *para*-directed disproportionation of potassium benzoate in Section 10.4. The last of these is known as the Henkel II process.

Unsurprisingly, the Henkel I process is related to the II process. It involves the isomerization of *o*-potassium phthalate to the *p*-isomer, in the presence of a zinc – cadmium catalyst at temperatures somewhat above 400°C and a modest pressure below 20 bar. Potassium is an expensive material and must be recovered. This can be done by reacting the potassium terephthalate with phthalic anhydride to yield more of the *o*-potassium phthalate.



Like *m*-xylene, *p*-xylene can be ammoxidized. Terephthalonitrile results, which can be hydrolyzed to terephthalic acid. This process is not in use. It is interesting that the ammoxidation is carried out without added oxygen, the vanadium pentoxide/ alumina catalyst giving up its oxygen in the process. The concept of an oxide as both a catalyst and a coreactant (a cataloreactant) for oxidations has been attempted by DuPont in a process for the oxidation of *n*-butane to maleic anhydride (Section 7.4.2) and in an unused process for aniline (Section 9.3).

11.3.3 Poly(ethylene terephthalate)

The formation of poly(ethylene terephthalate) was described in Section 5.7.1. The market patterns for poly(ethylene terephthalate) in the United States and Asia-Pacific differ markedly. Sixty-seven percent of U.S. consumption goes into bottles, compared

with Asia-Pacific's 18%. Twenty-eight percent goes into fibers compared with 78%, and 5% into film compared with 4%. Globally, fibers consume over 60% and bottles over 30%. Polyester is the world's third largest polymer with 18% of production, a share exceeded only by polyethylene and polypropylene.

Polyester fibers remain the growth area in Asia-Pacific but, in the United States, the demand has been for bottle resin, largely for containers for carbonated beverages. The polyester is biaxially oriented; that is, it is drawn in two dimensions by blowing, rather than in one dimension, as is the case when it is drawn into a fiber. It has sufficient mechanical strength to withstand the pressure in carbonated beverages, but it does not have sufficient resilience to withstand the sharp bend required at the bottom of the bottle. For this reason, the first bottles made from polyester had a hemispherical end, and the bottle was set into a polyethylene cup. A later version distributed the stresses created in making the sharp bend by molding a bottom comprising four convolutions, all of which have rounded edges. The elimination of the polyethylene makes recycling easier.

The significant properties of polymers are usually their mechanical characteristics – crystallinity, Young's modulus, glass transition temperature, and so on (Section 17.5). In the case of bottles for beer and carbonated beverages, however, the permeability of polymers to oxygen and carbon dioxide is crucial.¹⁶ The permeabilities of several polymers are shown in Table 11.3. HDPE and PVC are clearly unsuitable. PET is better, but beer in a 2-liter PET bottle at about 4.6 bar would lose about a third of its fizz in six months and would be oxidized more rapidly. This is acceptable for carbonated beverages, where oxidation is not a problem, and the level of fizz simply needs to be above a certain level. Carbon dioxide can be put in at 6 bar and any losses are unimportant. Nor is it a problem with less carbonated ("flat") highly flavored British beers, as long as the polymer is colored, because beer photodegrades. For light lager-style beers, however, it cannot compete with conventional glass bottles and aluminum cans, other than in fast-turnover venues such as sports stadiums, concert arenas, and swimming areas, where there is concern about safety of glass bottles. In 2009, global beer consumption was approximately 1.8 billion hectoliters and is expected to rise to 2.3 billion hectoliters by 2020; hence the "holy grail"

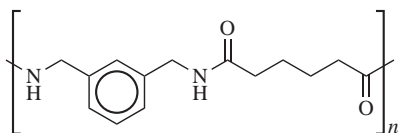
TABLE 11.3 Oxygen and Carbon Dioxide Permeabilities of Various Polymers

Polymer	Transmission of 25 μm Films (cm^3 per m^2 atmospheric pressure drop over 24 h)	
	Oxygen	Carbon Dioxide
High density polyethylene	2900	9100
Poly(vinyl chloride)	120	500
Poly(ethylene terephthalate)	95	240
Poly(vinylidene chloride)	10	75
Ethylene-vinyl alcohol (dry)	2	—
Ethylene-vinyl alcohol	100	—

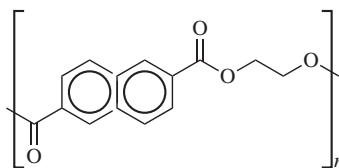
application for plastic bottles is beer containers. The soft drink bottle market is relatively stable in developed countries. Western Europe in 2008 consumed about 1 million metric tons of PET in bottles and growth was only 2% per year.

Numerous approaches for improving the shortcomings of homopolymer PET bottles are in place or under development. One solution is to make multilayer bottles using low permeability polymers such as ethylene-vinyl alcohol copolymer or poly(vinylidene chloride) (Section 5.11.7). The ethylene-vinyl alcohol copolymer is moisture sensitive, so it has to be sandwiched between two layers of PET.

Aluminizing the bottle also reduces gas transmission but prevents the consumer from seeing the product, which is one of the benefits of glass. Gas transmission through the cap has also been reduced by the use of a specialty nylon (MXD6 from *m*-xylylenediamine and adipic acid) rather than nylon 6 for the screw cap.



Nylon MXD6



Poly(ethylene naphthalate)

Copolymers (such as with terephthalic acid and naphthalene dicarboxylic acid), high barrier monolayers (such as poly(ethylene naphthalate)), and incorporation of oxygen scavengers in the plastic layers or in the cap lining have also been tried. The problems are the expense and the problems of recycling. PET homopolymer is readily recyclable; coated materials less easily so. Some recyclers have permission to use the recycled material in nonfood applications.

Worldwide, approximately 4.53 million tons of PET was collected for recycling in 2007. Petcore,¹⁷ the European trade association that fosters the collection and recycling of PET, reported that in Europe alone, in 2009, 1.4 million metric tons of PET bottles were collected – more than 48.4% of all bottles. In the United States, about 4 million metric tons of plastic bottles (HDPE and PET) were manufactured in 2009, of which 445,000 metric tons of HDPE bottles and 660,000 of PET bottles were recycled, a rate of 27.8%.¹⁸

Antimony trioxide or triacetate may be used catalytically in PET production, and concerns have been expressed that this could be a toxic hazard. Extraction levels, however, seem typically to be about 1% of the World Health Organization's "tolerable daily intake."

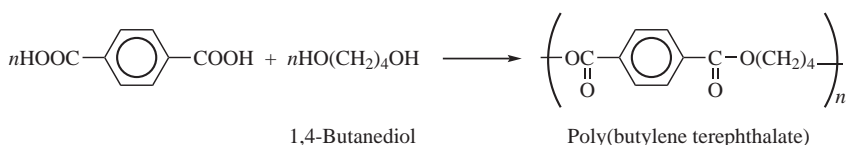
About 5% of poly(ethylene terephthalate) goes into a strong, biaxially oriented film known as Mylar. It is used in photographic and X-ray film, magnetic tapes for sound and video recordings, and containers for microwave and boil-in-the-bag cooking.

A small but growing amount of polyester is used as a molding compound. Because the polymer has a glass transition temperature of about 80°C, the molding does not crystallize well on cooling. Crystallization can be induced by nucleating the polymer,

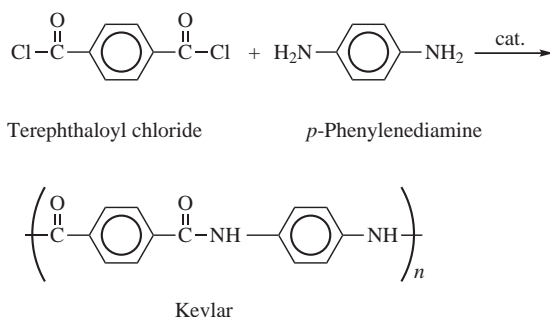
which makes molding possible only in specialized applications. Dimensional stability can also be achieved by addition of glass fiber.

11.3.4 Lower Volume Polymers from Terephthalic Acid

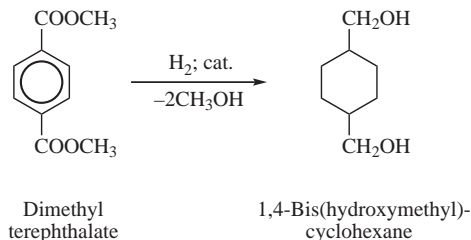
Poly(butylene terephthalate), made by condensing terephthalic acid or its dimethyl ester with 1,4-butanediol (Section 7.1.6.5), is a relatively inexpensive molding resin useful for pipe, automotive parts, and toothbrush bristles. It is also alloyed with polycarbonate to give a plastic useful for automobile bumpers and even for side panels.¹⁹



The condensation of terephthaloyl chloride with *p*-phenylene diamine leads to an aramid known as Kevlar. That it must be spun into fibers from concentrated sulfuric acid solution is an indication of its properties. The resulting fibers are stronger than steel fibers of the same dimension. Kevlar was probably the first of the liquid crystal polymers, a category of polymers whose rigid chains allow them to maintain a crystalline structure either in the melt form or in solution. It finds its major application as an asbestos replacement. Other uses include tire cord for large vehicles and reinforcement for bullet-proof vests and military helmets. It is used for canoe manufacture combined with epoxy resin, and as cloth for boat sails. Its most important use, however, was not anticipated by DuPont. Kevlar is the most important replacement for the now outlawed asbestos for brake linings, clutch facings, and related uses. Dyneema (Section 5.1.5) competes where temperature resistance is not required. Nomex (Section 11.2.1) is a polymer related to Kevlar.



Dimethyl terephthalate may be subjected to hydrogenolysis to convert the ester groups to alcohols. At the same time the ring is hydrogenated. 1,4-Bis(hydroxymethyl)cyclohexane, otherwise known as cyclohexane dimethanol, results.



This diol may exist in the *cis* or *trans* form, and the ratio must be carefully controlled if the product is to be used for the formation of polyester fibers by condensation with terephthalic acid. Eastman's "Kodel" contains this diol. It is also useful for the preparation of specialty polyurethane resins.

Both Shell and DuPont are pursuing commercialization of a new polyester resin, poly(trimethylene terephthalate), which is based on the polymerization of terephthalic acid and 1,3-propanediol (Sections 5.11.6.6). This material, particularly in carpet applications, combines the inherent stain resistance of polyester with the elastic recovery and resilience of nylon. It dyes more easily and is less abrasive. In March 2009, the Federal Trade Commission approved a subclass to traditional polyester called triexta, which is essentially poly(trimethylene terephthalate), and this reclassification should improve its marketability. Its cost depends crucially on the price of 1,3-propanediol.

ENDNOTES

1. The economics of xylenes production is discussed in Nexant ChemSystems PERP report 01/02-7, *Xylenes* (May 2002).
2. http://www.axens.net/html-gb/offer/offer_services_24.html.php.
3. http://www.axens.net/upload/news/fichier/ptq_spring2004.pdf.
4. Nexant ChemSystems PERP report 94/95S14, *meta-Xylene/Isophthalic Acid* (February 1997). highlights UOP's MX Sorbex process and Mitsubishi Gas Chemical's HF/BF₃ extraction process for separating and purifying *m*-xylene and production and uses for isophthalic acid.
5. <http://www.icis.com/v2/chemicals/9076143/phthalic-anhydride/process.html>.
6. *Chemical Week*, 11/18 April 2011, p. 27.
7. <http://www.eng.buffalo.edu/Courses/ce435/2001ZGu/PhthalatePlasticizers/PhthalatePlasticizersReport.htm> discusses the various points for and against DEHP.
8. H.R. 4040 – 110th Congress (2007): Consumer Product Safety Improvement Act of 2008, GovTrack.us (database of federal legislation). Retrieved 14 August 2009.
9. http://en.wikipedia.org/wiki/Phthalate#cite_note-endo-0.
10. <http://www.cpsc.gov/about/cpsia/chap/holt.pdf>.

11. R. Navarro, M. P. Perrino, M.G Tardajos, and H. Reinecke, *Macromolecules*, **43**, 2377–2381, 2010.
12. <http://www.epa.gov/greenchemistry/pubs/pgcc/winners/dgcall.html>.
13. <http://www.ccponline.com/pdfs/GrChemNomination09.pdf>; acs.confex.com/acs/green09/recordingredirect.cgi/id/537.
14. Nexant ChemSystems PERP report 01/02-4, *Terephthalic Acid* (December 2002).
15. Nexant ChemSystems PERP report 99/00S4, *Developments in PET Recycling* (July 2000).
16. D. Birkett, *Chem. Brit.*, **38**, 28, July 2002, and H. Hansler, *Chem. Ind.*, 2000, p. 429, deal especially with beer bottles. See also Nexant ChemSystems PERP report 00/01S1.
17. <http://www.petcore.org/content/petcore-publishes-pet-collection-figures-2009-european-pet-bottle-collection-increases-more->.
18. <http://plasticsnews.com/headlines2.html?id=20462>.
19. Nexant ChemSystems PERP report 98/99S6, *Polybutylene Terephthalate* (July 1999).

CHAPTER 12

Chemicals from Methane

So far we have described six natural gas and/or petroleum-derived products as raw materials for chemicals – ethylene, propylene, butadiene and the C_4 stream, benzene, toluene, and the xylenes. To complete the picture we must add methane.

The major source of methane is natural or associated gas (Section 4.16). It is also available from refinery gases that are usually used for fuel and not recovered for chemicals. Although there has been an “explosion” in the discovery of natural gas in many places the world, notably the Russian Federation and Qatar, and recent discoveries in the CIS, Venezuela, and Saudi Arabia, the reserves in North America between 1989 and 2009 dropped by about 3.8%. The reserves-to-production ratio, which had dropped from 11.5 to 9 years in the 1990s, rose to 11.3 years. The U.S. position will presumably increase sharply when the reserves of shale gas are included. The global reserves-to-production ratio stands steady at about 60 years, as it has for a generation. If necessary, methane may be synthesized from petroleum (Section 12.4.2) or coal (Section 14.5). It may also be obtained from anaerobic digestion of municipal solid waste – the so-called mining of landfill (Section 16.6.4) – and digestion of sewage sludge.

Many reserves of natural gas are located in regions far from where the gas is required – the so-called stranded natural gas (Section 3.2). It can be transported by pipeline as a compressed gas, an acceptable solution for distances less than 2000 km, or it can be liquefied and shipped in refrigerated tankers. In the latter case, it must be regasified on arrival at its point of use. In addition, there are three chemical solutions to the problem. The first is to convert the natural gas to synthesis gas, which is anyway the main chemical use of methane, and then to convert the synthesis gas to methanol. The methanol can be shipped as a liquid, which leads to a large reduction in shipping costs (Section 3.2). Second, the natural gas can be converted to gasoline in a so-called MTG plant (Section 12.5.2.4), and third, it can be converted to olefins in an MTO plant (Section 12.5.2.5). These last two involve prior conversion of the gas to synthesis gas and thence to methanol. Lesser uses of methane include chlorination, conversion to

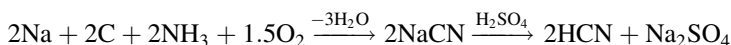
acetylene, and ammoxidation to hydrocyanic acid. Globally about 7% of methane is used as a chemical feedstock.

Waste natural gas (and hydrogen and other light hydrocarbons) are a product of petroleum refining and chemical plants, both of which have flare stacks where the gas is burned. The gas is a by-product of petroleum production and is not generally considered worth capture and sale. The stack is usually in a remote corner of the plant as a safety measure. The World Bank¹ estimates that over 150 billion m³ (112 million metric tons) of natural gas is flared or vented annually, an amount worth approximately \$30.6 billion, equivalent to 25% of U.S. gas consumption, 30% of the European Union's gas consumption, and half of Africa's gas consumption. It adds some 400 million metric tons/year to the anthropogenic carbon dioxide emissions.

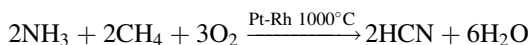
Satellite estimates indicate that gas flaring peaked at about 162 billion m³ in 2005 and declined to 140 billion m³ in 2008. The decrease in gas flaring corresponds to a reduction of some 60 million tons of CO₂ emissions between 2005 and 2008. The flaring is highly concentrated: Russia and Nigeria account for 40% of emissions; 10 countries account for 75%, and 20 for 90%.

12.1 HYDROCYANIC ACID

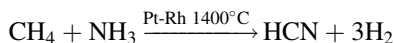
Hydrocyanic acid (hydrogen cyanide or HCN) was produced in the United States at a level of about 770,000 tons per year in 2002; growth has been slow. It was formerly made by the reaction of sodium, carbon (charcoal), and ammonia. In the first stage of the process, ammonia and sodium react to form sodamide, NaNH₂. This reacts with carbon to form sodium cyanamide, NaHCN₂, which in turn is reacted with more carbon to provide sodium cyanide, NaCN, at temperatures as high as 850°C. Yields based on sodium and ammonia were high. Acidification with sulfuric acid provided hydrocyanic acid.



The process has been superseded by the more economical Andrussov reaction between methane, air, and ammonia at 1000°C and slightly above atmospheric pressure over a platinum catalyst with 10–20% rhodium to prevent volatilization.



In a modified process used by DeGussa, air is omitted, and methane (or any other hydrocarbon feedstock including naphtha) reacts directly with ammonia at 1400°C.

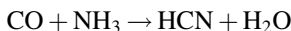


This provides one of the few examples in industrial chemistry of an intermolecular dehydrogenation and is possible because of the high temperature. Other examples

are provided by the interaction of benzene with ammonia (Section 9.3). and the condensation of two oleic acid molecules to form so-called dimer acid (Section 15.5).

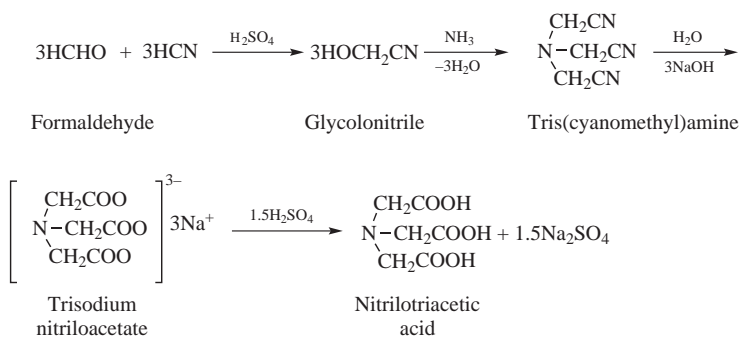
Hydrocyanic acid is also a by-product of the ammoxidation of propylene to acrylonitrile (Section 6.5). It was this lower cost source of the chemical that motivated the more economical methane-based route. By-product hydrocyanic acid enjoyed about 18% of the market in 2002.

Another route to hydrocyanic acid is the dehydration of formamide, a process that has been revived as a basic step in a synthesis of methyl methacrylate (Section 6.7.1). Hydrocyanic acid also results from the interaction of carbon monoxide and ammonia.



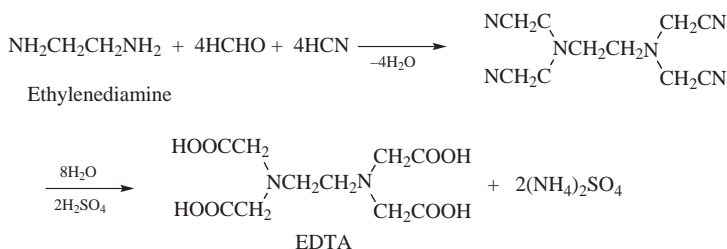
Hydrocyanic acid and its sodium salt undergo a number of industrially important reactions. Its largest application, hexamethylenediamine production, is described in Section 7.1.5. Its second largest use is for methyl methacrylate (Section 6.7.1). It has been used in two obsolete routes to acrylic acid (Section 6.4) and one to acrylonitrile (Section 6.5).

The powerful chelator, sodium nitrilotriacetic acid, is used to replace the sodium tripolyphosphate “builder” in some detergents. It is made from ammonia, methanol, and hydrocyanic acid. In the first step, 37% formaldehyde is reacted with HCN in the presence of sulfuric acid to give glycolonitrile. This reacts at 60°C with ammonia to give tris(cyanomethyl)amine. Hydrolysis with aqueous sodium hydroxide at 140°C and 3 bar at a pH of 14 gives sodium nitrilotriacetate. Treatment with sulfuric acid provides nitrilotriacetic acid.

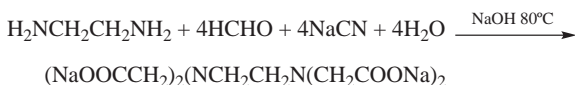


Its use as a builder in the United States has been inhibited because of the suggested toxicity of the chelates, of heavy metals such as iron, which could form in a washing machine. These are now believed to be nontoxic, and the product is one of the several phosphate replacements used more in Europe and in Canada than in the United States. The literature on where it is permitted is contradictory, and it may well be banned in the United States. Other builders include zeolites, which act as ion exchangers, and polyacrylic acids (Section 6.4). Phosphates are frowned upon because they lead to eutrophication in rivers and lakes (Section 20.4.4).

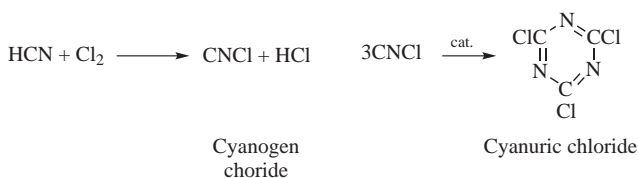
Other uses for hydrocyanic acid include conversion to sodium cyanide for gold recovery and preparation of ethylenediamine tetraacetic acid (EDTA). The latter is made via a modified Mannich reaction in which ethylene diamine is condensed with formaldehyde and hydrocyanic acid. Hydrolysis of the nitrile gives EDTA.



Single step processes are also used, either with sodium hydroxide or with an aqueous solution of sodium cyanide. In each instance the sodium salt results.

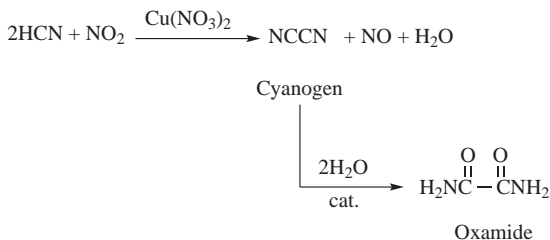


Another use for hydrogen cyanide is in the production of cyanuric chloride. Cyanogen chloride is first produced from chlorine and aqueous hydrocyanic acid at 40°C . The gas is trimerized to cyanuric chloride in the gas phase at over 300°C with activated charcoal and metal salts as catalysts. Cyanuric chloride is a starting material for the important triazine herbicides and fiber-reactive dyes. It is also used for the manufacture of triallyl cyanurate, for specialty polyesters, and for certain pharmaceutical syntheses.



An important use for hydrocyanic acid, or more frequently sodium cyanide, is in the synthesis of amino acids by the Strecker reaction. The most important application of this reaction is for the synthesis of DL-methionine, a poultry feed additive (Section 6.11.4).

Oxamide is a specialty fertilizer, not widely used, that releases ammonia slowly into the soil. It melts at 419°C without decomposition, making it one of the highest melting of all nonpolymeric organic compounds. It results from the hydrolysis of cyanogen, which in turn is made by the cupric nitrate catalyzed oxidation of hydrocyanic acid with nitrogen dioxide at $0\text{--}5^\circ\text{C}$.



The cyanogen hydrolyzes quantitatively with hydrochloric acid at room temperature. It has been proposed that the process be used with the by-product hydrocyanic acid from ammoxidation (Section 6.5). However, this use is precluded by the imbalance between fertilizer usage, which is very large, and hydrocyanic acid production, which is relatively small. Because fertilizers must be cheap, large capital investment in expensive hydrocyanic acid production is not warranted.

Hydrogen cyanide, absorbed on a diatomaceous earth such as celite, was the notorious Zyklon B used by the Nazis in their extermination camps. It boils at 25.6°C so that the solid pellets provided abundant vapor. Carbon monoxide was also used in gas chambers. At Auschwitz-Birkenau about 1.25 million people were gassed with Zyklon B – about 900,000 Jews together with 350,000 Poles, Russian prisoners of war, gypsies, and the disabled. Stutthof was another Zyklon B camp, while Majdanek used both hydrogen cyanide and carbon monoxide. All in all, about 3 million people were killed with cyanide, out of the 6 million Jews and 6 million non-Jewish civilians murdered by the Nazis.²

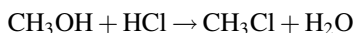
By an appalling irony, Zyklon B was developed for pest control at the Kaiser Wilhelm Institute, Berlin, by Walter Heerdt, assistant to the Institute's director, Fritz Haber. Haber subsequently was forced to flee Germany because of the Nazi race laws, and various of his relatives were gassed.

12.2 HALOGENATED METHANES

The markets for halogenated methanes have been reduced by concerns about the ozone layer (Section 20.4.1). The Montreal Protocol has banned many of them, and their manufacture is now largely of historical interest, although one must bear in mind that not all countries are signatories to the Protocol. Thus some halogenated methanes are still manufactured as intermediates on the route to less harmful compounds.

Chlorination of methane yields a mixture of mono-, di-, tri-, and tetrachloromethanes.³ These can be separated by distillation and this provides a route to their preparation, but it is not the preferred one. Chloromethane (methyl chloride) chlorinates more readily than methane, the formation of dichloromethane becoming significant after 18% of the methane has been converted to chloromethane. Indeed, a high conversion to chloromethane can be obtained only if the methane to chlorine

ratio is greater than 10:1. Consequently, the preferred route to chloromethane is the reaction of methanol with hydrogen chloride.

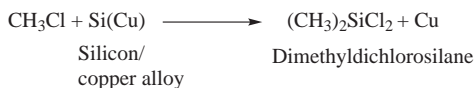


In contrast, chloroethane (ethyl chloride) can be made by the chlorination of ethane since dichlorination does not start until about 75% of chloroethane has been produced.

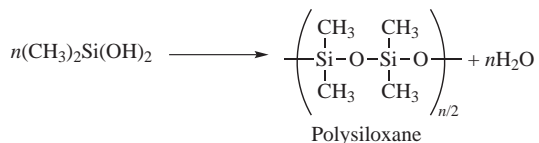
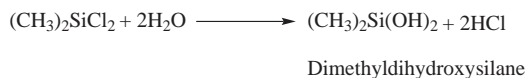
12.2.1 Chloromethane

In 2002 capacity for chloromethane was 243,000 tons in the United States.

Its major use in the past has been for conversion to dichloromethane (Section 12.2.2) whose use has declined markedly in the 1990s because of alleged toxicity. Today about 80% of chloromethane production is used to make silicone resins (or more appropriately polysiloxanes), which result from the hydrolysis of dimethyldichlorosilane. This monomer is made by reaction of chloromethane with silicon, which is usually in the form of a copper alloy.



The silane hydrolyzes with water to provide dimethyldihydroxysilane, which converts to a polysiloxane. Trimethylhydroxysilane from trimethylchlorosilane acts as a chain stopper.

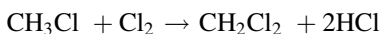


The type of organic groups attached to the siloxane backbone and the extent of crosslinking between the chains determines whether the silicone will be an oil, an elastomer, or a resin. Silicones are used in water-repellent coatings, mold release agents, and slip agents. They are formulated as elastomers, caulking compounds, and sealants and as resins for lamination with glass. Silicone oils are used as antifoam agents in detergents and in aerobic fermentation processes such as penicillin production.

A smaller volume use for chloromethane is in the preparation of methylcellulose (Section 16.4). Its use in the manufacture of tetramethyl and tetraethyl lead for gasoline has been phased out in the USA. Chloromethane is used in the preparation of quaternary ammonium compounds such as difatty dimethylammonium chloride (Section 15.3) and has a small use as a catalyst and solvent in the production of butyl rubber.

12.2.2 Dichloromethane

Dichloromethane (methylene chloride) is made by the chlorination of chloromethane. Further chlorination of the mixture of chlorinated methanes provides chloroform and carbon tetrachloride. Dichloromethane production in 2001 was estimated to be 91,000 metric tons, compared with 295,000 metric tons in 1996 and 276,000 metric tons in 1984.



Chloromethane

Dichloromethane

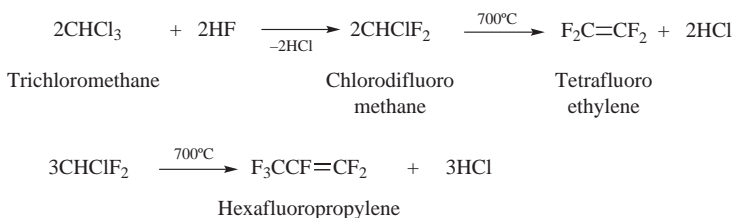
Dichloromethane has been used as a paint stripper, especially for jet aircraft, which must be stripped at intervals and examined for cracks. It had the advantage over alkaline paint removers of not attacking aluminum. On the other hand, many chlorinated hydrocarbons are health hazards. Dichloromethane is described as a possible carcinogen/mutagen but it is not nearly as dangerous as tri- and tetrachloromethane because its appreciable water solubility means it does not accumulate in body fat. Nonetheless, dichloromethane's use as a paint stripper has declined precipitously. The European Union in 2010 banned its use in paint strippers for consumers and many professionals. A substitute is *N*-methylpyrrolidone (Section 12.3.1). It has also been important in solvent degreasing, an application that is similarly being eliminated. Thirty-five percent of dichloromethane production was for synthesis of chlorofluorocarbons, which are being phased out, as is the application for solvent extraction of caffeine, cocoa, and edible oils. Production is nonetheless predicted to remain significant because of its use in the production of trichlorosilane and silicon tetrachloride, which are intermediates in the production of ultra-pure silicon for the semiconductor industry. These grew steadily in the 2000s.

12.2.3 Trichloromethane

Trichloromethane (chloroform) production in 1998 was 239,000 metric tons and increased to about 295,000 metric tons in 2002, because it is used in the production of hydrofluorocarbons, the replacements, if temporary, for fluorocarbons. It does, however, attack the liver and is carcinogenic in animals. On the basis of evidence of its mode of action, the EPA is trying to have it classified as a threshold carcinogen, so that tiny concentrations in water that has been disinfected with chlorine would still be acceptable (Section 19.7). Chloroform once appeared in toothpastes, cough syrups and ointments, but it has been banned as a consumer product in the United States since 1976. Cough syrups containing chloroform can still be legally purchased in pharmacies and supermarkets in the United Kingdom. It is still used as a laboratory solvent, being thought of as less toxic than carbon tetrachloride (tetrachloromethane).

Trichloromethane is made by chlorination of either methane or chloromethane. The chlorination of methane can be carried out either thermally with chlorine without catalysts or by oxychlorination (Section 5.4) with oxygen, hydrogen chloride, and a potassium chloride/cupric chloride catalyst. Both processes are highly exothermic. The oxychlorination is carried out at 400–450°C at slightly elevated pressure. The chlorination may be initiated by photons or by chlorine atoms formed when chlorine molecules are heated. Trichloromethane was once an important anesthetic.

At one time, 97% was used for production of chlorofluorocarbon refrigerants and aerosol propellants, applications that have been phased out (Section 20.4.1). Meanwhile trichloromethane reacts with hydrofluoric acid as noted above to give chlorodifluoromethane which, on pyrolysis at 700°C, gives tetrafluoroethylene and hexafluoropropylene. The former is the monomer for Teflon. The reaction is catalyzed by antimony pentafluoride.



12.2.4 Fluorocarbons

Fluorocarbons can be made from both chloroform and carbon tetrachloride by stepwise displacement of the chlorine atoms with hydrofluoric acid (HF). The higher the temperature and pressure, the more substitution results. Thus tetrachloromethane yields CFCl_3 , CF_2Cl_2 , and CF_3Cl ; trichloromethane yields CHFC_2 , CHFCl_2 , and CHF_3 . Catalysts for the reactions are fluorides or oxyfluorides of aluminum or chromium. All except CHF_3 are now banned. Class one ozone depleters are shown in Table 12.1. These were the first to be phased out.

Hydrofluorocarbons and fluorinated ethers are potential replacements. They contain fluorine and hydrogen, but no chlorine or bromine in most instances. In some replacements, a reduced number of chlorine atoms is considered acceptable, but their use is considered a temporary measure, and they are intended to be phased out fairly quickly, by 2020 in developed countries and 2030 in developing countries. The replacements are shown in Table 12.2. There is some evidence, however, that China and Brazil are increasing rather than phasing out their consumption of ozone depleters.⁴ In addition, the replacement hydrofluorocarbons appear to be infrared absorbers that contribute to global warming.

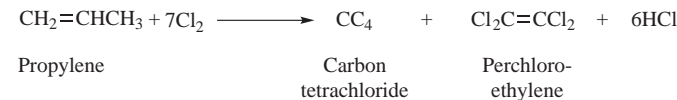
12.2.5 Tetrachloromethane and Carbon Disulfide

Tetrachloromethane (carbon tetrachloride) was the raw material for trichlorofluoromethane and dichlorofluoromethane, discussed above and now phased out. It has no

TABLE 12.1 Class I Ozone Depleting Substances

CFC-11 (CCl ₃ F)	CFC-212 (C ₃ F ₂ Cl ₆)
Trichlorofluoromethane	Hexachlorodifluoropropane
CFC-12 (CCl ₂ F ₂)	CFC-213 (C ₃ F ₃ Cl ₅)
Dichlorodifluoromethane	Pentachlorotrifluoropropane
CFC-113 (C ₂ F ₃ Cl ₃)	CFC-214 (C ₃ F ₄ Cl ₄)
1,1,2-Trichlorotrifluoroethane	Tetrachlorotetrafluoropropane
CFC-114 (C ₂ F ₄ Cl ₂)	CFC-215 (C ₃ F ₅ Cl ₃)
Dichlorotetrafluoroethane	Trichloropentafluoropropane
CFC-115 (C ₂ F ₅ Cl)	CFC-216 (C ₃ F ₆ Cl ₂)
Monochloropentafluoroethane	Dichlorohexafluoropropane
Halon 1211 (CF ₂ ClBr)	CFC-217 (C ₃ F ₇ Cl)
Bromochlorodifluoromethane	Chloroheptafluoropropane
Halon 1301 (CF ₃ Br)	CCl ₄ Carbon tetrachloride
Bromotrifluoromethane	
Halon 2402 (C ₂ F ₄ Br ₂)	Methyl chloroform (C ₂ H ₃ Cl ₃)
Dibromotetrafluoroethane	1,1,1-trichloroethane
CFC-13 (CF ₃ Cl)	Methyl bromide (CH ₃ Br)
Chlorotrifluoromethane	
CFC-111 (C ₂ FCl ₅)	CH ₂ Br ₂
Pentachlorofluoroethane	
CFC-112 (C ₂ F ₂ Cl ₄)	HBFC-12B1 (CHF ₂ Br)
Tetrachlorodifluoroethane	
CFC-211 (C ₃ FCl ₇)	CH ₂ BrCl
Heptachlorofluoropropane	Chlorobromomethane

alternate uses. In the twentieth century, it was used as a dry cleaning solvent and a refrigerant, but was displaced because of its toxicity and because, in a fire, it would decompose giving phosgene. It may be made by exhaustive chlorination of methane or chloromethane, but there are two more important routes. The most widely used is a “two-for-one” reaction that produces both tetrachloromethane and perchloroethylene by the chlorolysis of a propane–propylene mixture at about 500°C:



The quantity produced is dependent on the demand for perchloroethylene. In the days when carbon tetrachloride was more widely used, the shortfall was made up by a route starting with methane but proceeding via carbon disulfide, an important methane-based chemical. An iron catalyst at 30°C brings about the chlorination:

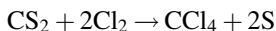
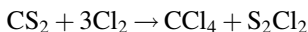


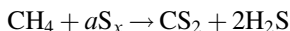
TABLE 12.2 Applications and Replacements for Fluorocarbons

Application	Previously Used CFC	Replacement
Refrigeration and air-conditioning	CFC-12 (CCl_2F_2)	HFC-23 (CHF_3)
	CFC-11 (CCl_3F)	HFC-134a (CF_3CFH_2)
	CFC-13 (CClF_3)	HFC-507 [a 1:1 azeotropic mixture of HFC-125 (CF_3CHF_2) and HFC-143a (CF_3CH_3)]
	HCFC-22 (CHClF_2)	HFC-410 [a 1:1 azeotropic mixture of HFC-32 (CF_2H_2) and HFC-125 (CF_3CHF_2)]
	CFC-113 ($\text{Cl}_2\text{FCCClF}_2$)	
	CFC-114 ($\text{CClF}_2\text{CClF}_2$)	
Propellants in medicinal aerosols	CFC-115 (CF_3CClF_2)	
	CFC-114 ($\text{CClF}_2\text{CClF}_2$)	HFC-134a (CF_3CFH_2)
Blowing agents for foams		HFC-227ea ($\text{CF}_3\text{CHFCF}_3$)
	CFC-11 (CCl_3F)	HFC-245fa ($\text{CF}_3\text{CH}_2\text{CHF}_2$)
	CFC 113 ($\text{Cl}_2\text{FCCClF}_2$)	HFC-365 mfc ($\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$)
Solvents, degreasing agents, cleaning agents	HCFC-141b (CCl_2FCH_3)	
	CFC-11 (CCl_3F)	None
	CFC-113 ($\text{CCl}_2\text{FCClF}_2$)	

Excess chlorine gives sulfur monochloride, also of interest industrially:



Carbon disulfide is made by reaction of methane and sulfur vapor in the presence of a catalyst:

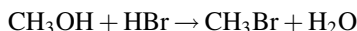


where $ax = 4$ and x is between 2 and 8 since it is an equilibrium mixture of S_2 , S_6 , and S_8 .

A major use for carbon disulfide is in the manufacture of regenerated cellulose for rayon, cellophane, and synthetic sponges (Section 16.4), all mature products.

12.2.6 Bromomethane

Bromomethane (methyl bromide) is made from methanol and hydrobromic acid:



or from methanol plus bromine and a reducing agent.

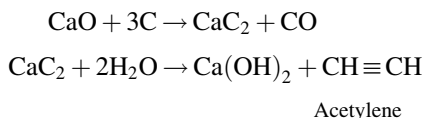
World production in 1998 was 61,436 metric tons. It also occurs naturally. In the ocean, marine organisms are estimated to produce 1–2 million metric tons annually.⁵

It is manufactured for agricultural and industrial use by reaction of methanol with hydrogen bromide. It was widely used as a soil and grain fumigant and less widely to fumigate private residences infested with termites. It was a latecomer to the list of chemicals believed to affect the ozone layer. It was phased out in the United States by January 2005 but is still used in Chile. It is considerably safer and more effective than most other soil sterilants, and its loss to the seed industry has resulted in changes to cultural practices. There is increased reliance on soil steam sterilization, mechanical rogueing (freeing from inferior plants or seedlings), and fallow seasons. As nature produces it on a large scale, one has to wonder about the cost-effectiveness of preventing industrial synthesis (Section 20.4.1).

12.3 ACETYLENE

Acetylene rose in importance as a chemical feedstock after World War II and reached a peak in the mid-1960s. Its use in the developed world has since declined precipitously. Coal was not only a source of aromatics, by way of coke oven distillate (Chapter 9), but was also the raw material for acetylene and hence the source of many early plastics and aliphatic organic chemicals.

In the oldest process, coke and lime are heated in an electric furnace to 2000°C to give calcium carbide. This is hydrolyzed by water to give acetylene.



The process has many of the characteristics of nineteenth century industry. It is a batch process. It is labor intensive because of the handling of solids, and energy intensive because of the electric furnace. It is environmentally unattractive because every ton of acetylene produced is accompanied by 2.8 tons of calcium hydroxide, usually in a slurry with 10 times as much water. The capital cost of the furnace is high and it has a short life because of the “heroic” conditions used.

Even in the days of cheap energy, the problems with the carbide process provided an impetus for its replacement. In the early 1960s, many attempts were made to derive acetylene from petroleum. Thermodynamically, it is the stable C₂ hydrocarbon above 1300°C, but the pyrolysis of other hydrocarbons is not so simple. It is difficult to quench the reaction mixture rapidly enough to prevent reverse reactions and to keep residence times short enough to prevent coking. Separation of acetylene from by-product hydrogen provides an additional problem.

These difficulties were addressed in the Wulff and Sachsse processes, which in theory can start with naphtha or natural gas. The naphtha-based plants, mainly European, gave continuous trouble and were closed after short lives.

Today there are four sources of acetylene. The calcium carbide route is one, but much of U.S. acetylene produced in this way is for the nonchemical application of arc welding. Calcium carbide has played an honorable role in the history of the U.S. chemical industry and even gave its name to the Union Carbide Corporation, whose name disappeared when the company was absorbed by Dow. Its derivative, calcium cyanamide, gave its name to the American Cyanamid Corporation, a veteran U.S. chemical company that split into Cytec and American Cyanamid in 1994. Its name disappeared when the latter was taken over by American Home Products. Carbide's energy requirements, however, mean that, until recently, the general view was that it could only be made economically in countries such as Norway, which have cheap hydroelectric power, and unproductive land where the waste calcium hydroxide can be dumped.

For most chemical processes in the United States, acetylene is obtained from three other sources. The first is as a by-product from steam cracking (Section 4.5.1). The cracking of propane at high severity, that is, high temperatures, can yield up to 2% of acetylene. Such conditions also produce a maximum amount of ethylene. Steam cracking of ethane/propane accounts for about half of U.S. acetylene production. Before the C_2 fractionation, the acetylene in the C_2 stream is selectively absorbed in dipolar aprotic solvents such as dimethylformamide or *N*-methylpyrrolidone. If the acetylene is not wanted, it must be selectively hydrogenated to ethylene, and most crackers operate in this way.

A second process is thermal, the above-mentioned Wulff process, operated not with naphtha but with natural gas. The reactor consists of a furnace containing a hot brick lattice. The bricks are heated for a minute to about 1300°C by burning a gaseous fuel. The feed methane is then pyrolyzed for 1 minute. The same sequence of operations is then carried out in the opposite direction through the furnace, giving a 4-minute cycle with a final temperature below 400°C . The product is quenched and comprises a mixture of acetylene and ethylene in a ratio of 1:2.

The third process requires oxygen and is known as the partial oxidation process. There are several variations, but the Sachsse process is the most important of them. Methane and oxygen are preheated to 600°C and reacted in a special burner with flame formation. A temperature of about 1500°C is achieved. After a residence time of a few milliseconds, the mixture is quenched to 40°C with water or quench oil to inhibit soot and hydrogen formation. This yields a gaseous product containing 8–10% acetylene, corresponding to 30% of the carbon in the feedstock. Synthesis gas (Section 12.4) is the major product and about 1.5% of the initial carbon emerges as soot.

The Wulff and Sachsse processes, although not as hostile as the Carbide process, are energy intensive. Thus acetylene has become steadily more expensive in comparison with ethylene, and almost everything that used to be done with acetylene can now be done more cheaply with olefins.

An impressive range of chemicals has been made from acetylene in the past – vinyl chloride from acetylene and hydrogen chloride; vinyl acetate from acetylene and acetic acid; acrylonitrile from acetylene and hydrocyanic acid; acetaldehyde from acetylene and water; neoprene from acetylene dimer (vinylacetylene) and HCl; acrylate esters by way of acetylene, an alcohol, and carbon monoxide; and

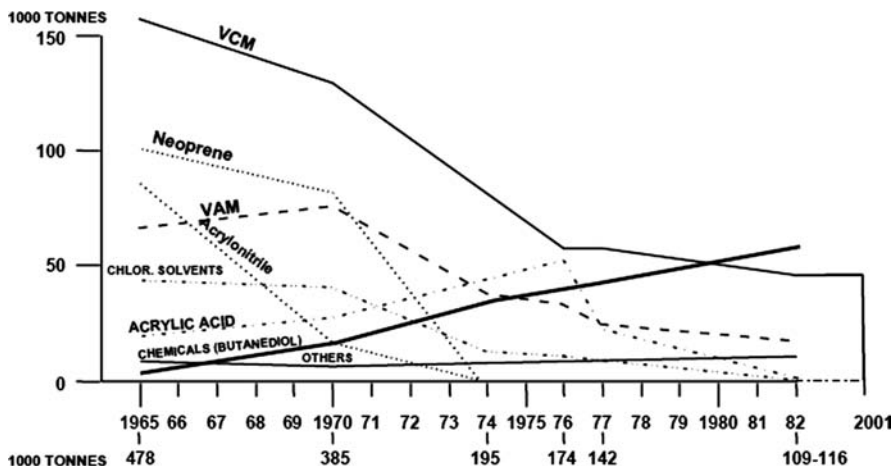


FIGURE 12.1 Decline of acetylene-based processes in the United States, 1965–2001. VCM = vinyl chloride; VAM = vinyl acetate. (Source: Nexant Inc.)

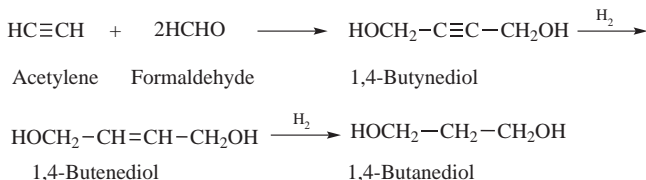
perchloroethylene (Section 12.3.2) by a multistage chlorination–dehydrochlorination process. But the processes became obsolete until the Chinese revived them (see below). In the United States, between 1967 and 1974, 25 acetylene plants closed, and acetylene consumption for chemical use dropped from 560,000 metric tons to 180,000 metric tons between 1962 and 1977. In 2000, acetylene demand was estimated at about 136,000 metric tons, and in 2002 the supply dropped to under 90,000 metric tons as Borden closed its acetylene-based VCM plant and ISP shuttered its two 1,4-butanediol plants in the United States (see below). The decline of the various acetylene-based processes is shown in Figure 12.1.

Meanwhile, such processes have been revived in China. China has abundant accessible coal and little oil. It also has a limitless supply of cheap labor and little concern with health and safety legislation. The cost of crude oil has risen. China has wide experience with coal technology and is making vinyl chloride from acetylene at acceptable economics. It is suggested that the acetylene route to acrylonitrile, and perhaps to other bulk chemicals, would be similarly viable. This perhaps depends as much on political as technological factors.⁶

The major area for the remaining acetylene use in the developed world is in Reppe chemistry. Reppe was a German chemist who studied the interaction of acetylene with aldehydes, ketones, alcohols, and carbon dioxide, during World War II. The acrylate process mentioned above (Section 6.4) is a Reppe reaction, as is the 1,4-butanediol process below.

12.3.1 1,4-Butanediol and 2-Methyl-1,3-propanediol

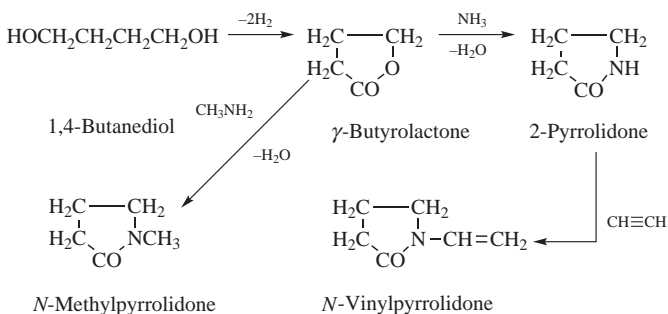
Acetylene reacts with formaldehyde to give 1,4-butanediol, which may be hydrogenated stepwise to butenediol and butanediol.



The condensation of 37% aqueous formaldehyde and acetylene takes place at about 100°C and 5 bar in the presence of a cuprous acetylide catalyst deposited on magnesium silicate. In this process, the formation of by-product propargyl alcohol $\text{CH}\equiv\text{CCH}_2\text{OH}$ is minimized. The subsequent hydrogenation is carried out in two stages because a purer product results. The first stage is operated at 50–60°C at 7–15 bar with a Raney nickel catalyst to yield 1,4-butenediol, which found application in the manufacture of the pesticide Endosulfan (Section 8.3). The second stage requires a temperature of 120–140°C with hydrogen at 150–200 bar with a nickel–copper–manganese catalyst on a silica gel carrier to yield 1,4-butanediol.

About 35% of 1,4-butanediol production is converted to tetrahydrofuran. This is converted to poly(tetramethylene ether glycol) in the same way that ethylene oxide can be converted to poly(ethylene oxide). The product is used in the formulation of polyurethanes and elastomeric fibers such as Spandex and a thermoplastic elastomer, Hytrel (Section 17.3.8).

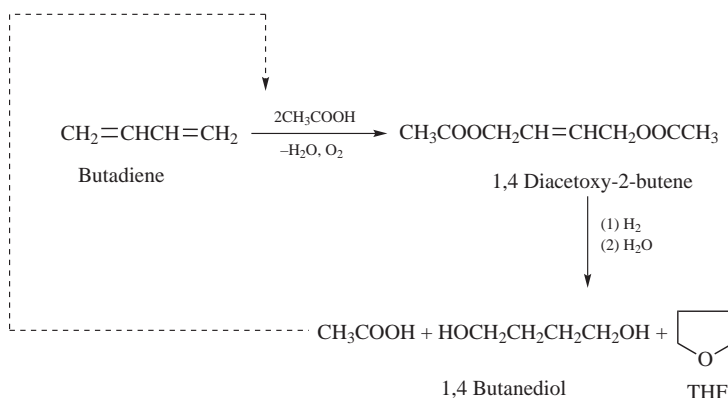
1,4-Butanediol is used as such in specialized polyurethane compositions for the manufacture of wheels for skates. It is also the basis for the so-called acetylenic chemicals γ -butyrolactone, pyrrolidone, and *N*-vinylpyrrolidone. γ -Butyrolactone is an aprotic solvent with limited end-use applications and some notoriety as a “date rape” drug. The great majority of γ -butyrolactone is converted to 2-pyrrolidone or *N*-methylpyrrolidone, a replacement for chlorinated solvents.⁷



2-Pyrrolidone’s major use is for conversion to *N*-vinylpyrrolidone. This can be polymerized to poly(*N*-vinylpyrrolidone) or copolymerized with vinyl acetate. These polymers are formulated into hair sprays, used as excipients in pharmaceutical pill manufacture, and as clarifying agents for beer and wine. During World War II poly(*N*-vinylpyrrolidone) was of interest in Germany as a replacement for blood

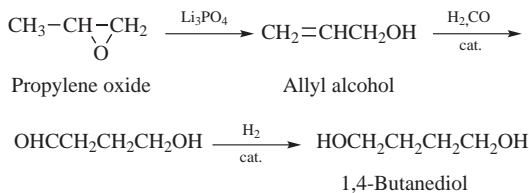
plasma. The other important use for 1,4-butanediol is in the formulation of poly (butylene terephthalate) (Section 11.3.4).

1,4-Butanediol has a modest but growing market. The U.S. production rose from about 390,000 metric tons in 2002 to 1,300,000 metric tons in 2010. Numerous possible routes to it have been developed. In 1979 in Japan, Mitsubishi Chemical commercialized a process from butadiene by an acetoxylation, reminiscent of an unsuccessful process for the manufacture of ethylene glycol (Section 5.7.2). The acetoxylation proceeds more readily with the conjugated butadiene than with ethylene because the double bond system is more reactive (Section 5.7.1). Thus it is possible to use a palladium–tellurium catalyst without the iodine promoter required for ethylene, alleviating much of the corrosion, which was the Achilles heel of the earlier process. After the initial acetoxylation, the 1,4 diacetoxy-2-butene is hydrogenated to 1,4-diacetoxybutane, which is saponified to the desired product and acetic acid for recycle.



As indicated above, this process can also be run to give tetrahydrofuran (THF) as the major product. BASF licensed this process in 2000 for a new plant in South Korea.

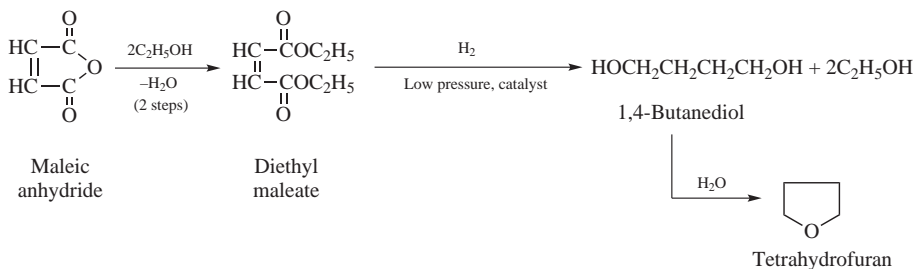
Another process for 1,4-butanediol production, commercialized in the United States by ARCO Chemical (now LyondellBasell) in 1990, starts with propylene oxide, which may be isomerized to allyl alcohol with a lithium phosphate catalyst. This was a step in an obsolete glycerol process (Section 6.11.2). Hydroformylation of the allyl alcohol yields an aldehyde, which on hydrogenation gives 1,4-butanediol.



The hydroformylation is difficult and does not provide maximum selectivity to a linear product. Thus the branched aldehyde $\text{CH}_3\text{CH}(\text{CHO})\text{CH}_2\text{OH}$ forms, which on

hydrogenation provides a coproduct, 2-methyl-1,3-propanediol, $\text{CH}_3\text{CH}(\text{CH}_2\text{OH})_2$. LyondellBasell successfully developed markets for this new diol. About 25% is used as a solvent glycol in personal care products (neutralizer, emollient, emulsifier, and humectant) and the remainder in the manufacture of resins and coatings. The two primary hydroxyl groups react with acids and acid anhydrides to yield polyesters. With aromatic acids (isophthalic, terephthalic, and phthalic anhydride) hard, unsaturated polyester resins are formed, which are used in applications such as bathroom countertops and tubs, as well as boat manufacture. Polyester polyols, formed by reaction with adipic acid, are used in polyurethane formulations for the coatings industry.

A process developed by Davy McKee and instituted in Japan in 1993 starts with maleic anhydride (Section 7.4.2), which is converted to diethyl or dimethyl maleate in two steps. This unsaturated ester is hydrogenated and subjected to hydrogenolysis in one step to give the desired product and ethanol for recycle.



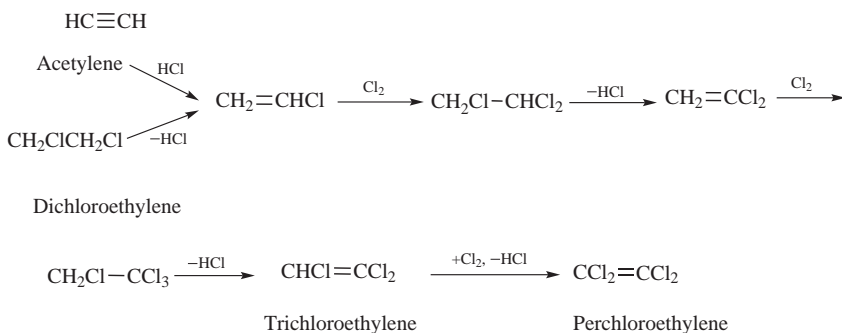
A DuPont process, for which a plant was completed in Spain in 1995, makes possible the conversion of maleic anhydride to tetrahydrofuran in one step. The major use for 1,4-butanediol is for conversion to tetrahydrofuran (THF), hence the DuPont process accomplishes in one step what the Davy McKee process does in four steps. The DuPont process entails hydrogenolysis of an aqueous solution of maleic acid. Besides the desired THF, a range of intermediate products, including succinic acid, γ -butyrolactone, and 1,4-butanediol is formed. Since some unreacted maleic acid is always present, the 1,4-butanediol undergoes acid catalyzed cyclic dehydration to give additional THF. The unreacted maleic acid, succinic acid, and γ -butyrolactone are recycled back to the hydrogenolysis reactor. BP and Lurgi have combined to develop a similar process which converts *n*-butane to an unisolated maleic acid intermediate and then to 1,4-butanediol and/or THF. BP has built a plant using this technology in Lima, Ohio. In the mid-1990s, Sisas, a small Italian entrepreneurial company, developed and operated a process that converted maleic anhydride to γ -butyrolactone in one step. The butyrolactone was then converted to 1,4-butanediol, THF or *N*-methyl pyrrolidone depending on market requirements. Sisas ran into financial difficulty and BASF bought the Sisas assets in 2001. They also built a plant in Caojing, Shanghai, which went on stream in 2005. It was scheduled to make 80,000 metric tons/year of THF and, from it, 60,000 metric tons/year of polyTHF.

[poly(tetramethylene ether glycol)]. This was butane based, via maleic anhydride. It was initially mothballed, but 30,000 metric tons per year capacity was added in 2007, and the new, 1,4-butanediol-based plant was opened in 2008. Thus BASF now operates 1,4-butanediol or THF plants based on acetylene (United States and Germany), butadiene (Malaysia), and *n*-butane (Belgium and Caojing). THF is widely used as a solvent for pharmaceuticals.

Genomatica has genetically engineered a microbe that will convert sugars to 1,4-butanediol in a single step.⁸ A 3000 liter pilot plant has been operating since 2010; a full scale plant is promised in 2012. It is claimed that Bio-BDO will be less expensive, require about 60% less energy, and produce 70% less carbon dioxide emissions than BDO made from natural gas. Tate & Lyle, M & G (a major European chemicals producer), Waste Management, and Mitsubishi Chemical are collaborators.

12.3.2 Lesser Uses for Acetylene

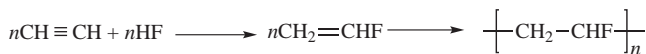
Trichloroethylene (for degreasing) and perchloroethylene (for dry cleaning) may be made from acetylene. Most perchloroethylene, however, is produced from simultaneous chlorination and pyrolysis of hydrocarbons or by oxychlorination of ethylene dichloride (Section 5.11.7).



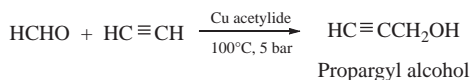
Both products suffer from the same ecological problems as other chlorinated compounds, and their consumption decreased from the early 1990s onwards.

The demand for trichloroethylene as a degreaser began to decline in the 1950s in favor of the less toxic 1,1,1-trichloroethane. However, 1,1,1-trichloroethane production has been phased out in most of the world under the Montreal Protocol, and as a result trichloroethylene has experienced some resurgence in use as a degreaser. Trichloroethylene is also used in the manufacture of a range of fluorocarbon refrigerants such as 1,1,1,2-tetrafluoroethane (HFC 134a). Philadelphia is phasing out perchloroethylene and propyl bromide from dry cleaners by the end of 2013.⁹

Vinyl fluoride results from the addition of hydrogen fluoride to acetylene (Section 5.11.8). It can be polymerized to poly(vinyl fluoride), a specialty polymer, with outstanding weathering properties.

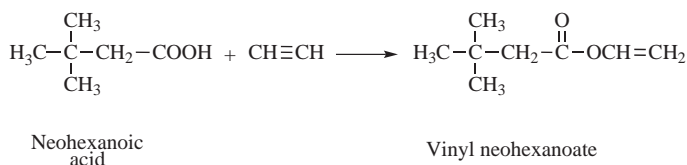


Partial carbonylation of acetylene with formaldehyde gives propargyl alcohol, used in the petroleum and metallurgical industries and as an intermediate in the manufacture of the miticide, propargite; the antibacterial, sulfadiazine, and various propargyl carbonate fungicides:

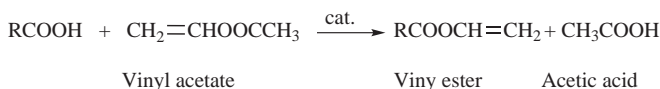


Higher carbonyl compounds also give acetylenic alcohols, and these form part of synthetic routes to terpenes, vitamins A and E, and various perfumes and steroids.

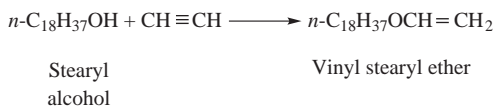
Other small uses for acetylene include vinyl ester formation by the zinc or mercury salt-catalyzed reaction between an acid and acetylene. Thus the so-called neo or Koch acids may be converted to vinyl esters as may fatty acids such as stearic or oleic.



Vinyl esters may also be made by an exchange reaction or transvinylation between an acid and a vinyl compound such as vinyl acetate or vinyl chloride. The major use of these materials is as internal plasticizers or modifiers for polymers based on vinyl chloride and vinyl acetate, to provide enhanced water resistance.



In a related reaction vinyl ethers result from the interaction of alcohols and acetylene. The reaction is catalyzed by alkali. These too are used as comonomers for the modification of vinyl polymers.



12.4 SYNTHESIS GAS

Synthesis gas is the name given to a variety of mixtures of carbon monoxide and hydrogen or nitrogen and hydrogen. It is made from methane from natural gas, if the

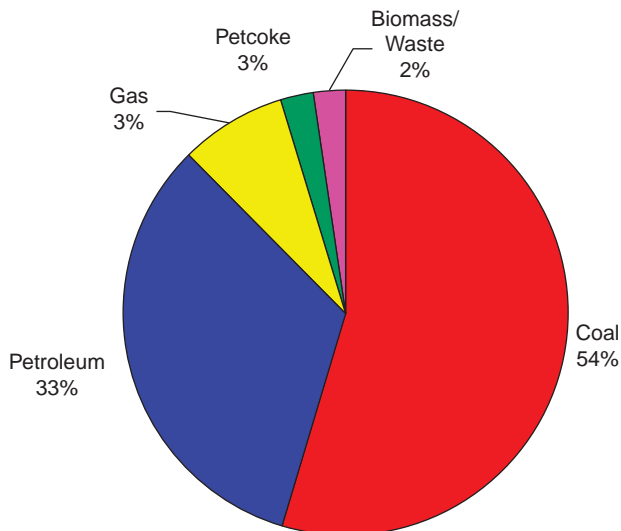


FIGURE 12.2 Global synthesis gas production by feedstock.

latter is available as it is in the United States and most of Europe. Countries lacking natural gas (e.g., Israel until recent discoveries and Japan) make synthesis gas from naphtha. It may, however, be made from virtually any hydrocarbon (e.g., so-called resid, the residue from petroleum distillation). Indeed, it may be made from almost any carbonaceous material including coal, peat, wood, biomass, agricultural residues, and municipal solid waste. The global sources of synthesis gas in 2007 are shown in Figure 12.2, which indicates the continuing importance of coal to the developing world chemical industry. Forty-seven percent of world ammonia capacity of 200 million metric tons was in Asia and 58% of that was in China.

Coal was an important feedstock prior to 1960. During World War II, it was used in Germany to provide synthesis gas for the manufacture of fuel and chemicals by the Fischer–Tropsch process (Section 14.2). The same technology is applied today in South Africa and makes coal the basis for at least half of that country’s energy needs. Coal is also gasified in China.

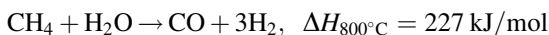
Different applications for synthesis gas require different mixtures. The Fischer–Tropsch reaction and methanol manufacture require $\text{CO}:\text{H}_2 = 1:2$; hydroformylation (the oxo process, Section 6.9) requires $\text{CO}:\text{H}_2 = 1:1$ and the Haber process for ammonia requires $\text{N}_2:\text{H}_2 = 1:3$ with no carbon monoxide. Other organic chemical syntheses require pure hydrogen. Properly adjusted, nonetheless, the basic synthesis gas processes can give all these mixtures.

12.4.1 Steam Reforming of Methane

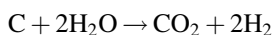
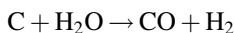
The most widely used synthesis gas process is the steam reforming of hydrocarbons, with partial oxidation of hydrocarbons as another possibility. Coal-based routes are

also of significance and will be described in Section 14.2. The dominant process is the steam reforming of methane.

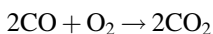
Before steam reforming can take place, the methane feedstock is desulfurized by passage over a zinc oxide catalyst at 360–400°C. Sulfur levels less than 2 ppm are required if the nickel steam-reforming catalyst is to have an adequate life. The methane is then mixed with steam in a molar ratio of between 2.5 and 3.5 of steam per mole of methane and passed over an alkali-promoted nickel catalyst, supported on potassium oxide or alumina. The reaction is carried out at about 800°C and 35 bar; it is endothermic and the heat is supplied externally. The principal reaction is



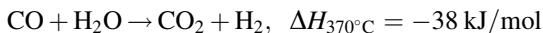
The exit gases contain about 7% unchanged methane plus some carbon dioxide and traces of the nitrogen present in the natural gas. The excess steam minimizes coking of the catalyst. The higher the steam:carbon ratio, the higher the CO_2 :CO ratio in the products.



If the synthesis gas is to be used to make ammonia, nitrogen must be added and carbon monoxide removed. This is done by addition of an amount of air calculated to provide a N_2 : H_2 ratio of 1:3. The oxygen in the air reacts with some of the carbon monoxide to give carbon dioxide.



The gases then pass to a second reforming unit at 370°C, possibly with additional steam. In the presence of an iron oxide catalyst, the water–gas conversion or shift reaction takes place.



These reactions are summarized in Figure 12.3.

The product gases contain hydrogen, nitrogen, carbon dioxide, and traces of methane, carbon monoxide, and argon. They are compressed and scrubbed with aqueous ethanolamine and diethanolamine (a variety of other processes are available) to remove carbon dioxide. Some of the carbon dioxide dissolves in the water – at high pressure, the solubility is high – and some reacts with the amine to give an unstable salt. The ethanolamine may then be recovered by steam stripping, which decomposes the salt. A further shift reaction may improve yields, and other processes are employed to reduce carbon monoxide to a very low level. The product is then delivered to an ammonia plant.

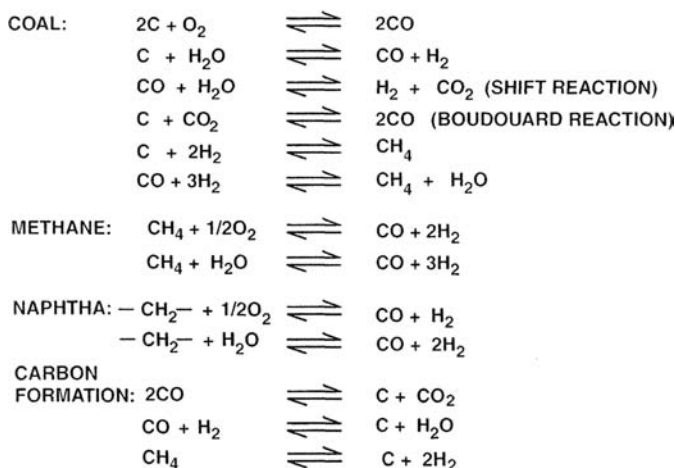
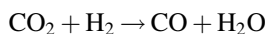


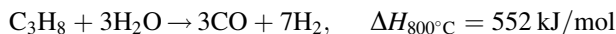
FIGURE 12.3 Important reactions in synthesis gas formation.

12.4.2 Variants of Steam Reforming

If synthesis gas is required for other purposes, the addition of nitrogen is not necessary. The shift reaction will then give CO/H_2 mixtures rich in hydrogen, or it will even give pure hydrogen. Alternatively, if carbon monoxide-rich materials are needed, then carbon dioxide may be added at the shift conversion stage so that the equilibrium in the shift reaction is pushed to the left and, instead of carbon monoxide converting water to hydrogen, the reverse occurs.

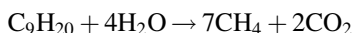


There are many variants to this process. Propane or naphtha may be the feedstock. With propane as the example, the following occurs.



If a higher steam: hydrocarbon ratio is used, the product has a higher $\text{CO}:\text{H}_2$ ratio than is possible with methane. It is thus less suitable for ammonia. Flexibility is achieved, however, by adjustment with the shift reaction.

In a further application of the steam reforming reaction, methane rather than synthesis gas is produced. It may be obtained fairly readily from any hydrocarbon feedstock that can be vaporized, for example, naphtha. The process is operated at a lower temperature than if synthesis gas is required. Typically, with nonane as an example,



The product is called substitute natural gas (SNG). The process was used in the United Kingdom before North Sea discoveries and is still used in Japan, where natural gas is lacking. Various processes are available to give methane from heavier hydrocarbon feedstocks, but the huge discoveries of natural gas in the former Soviet Union in the early 1980s and subsequent finds mean that oil is now thought likely to be depleted before natural gas. Hence interest in SNG from oil has diminished.

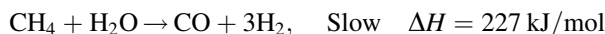
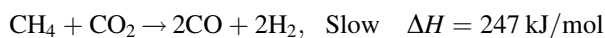
12.4.3 Partial Oxidation of Hydrocarbons

A second route to synthesis gas is partial oxidation of carbonaceous materials reacted with steam. If the feedstock can be vaporized, the reactions are carried out simultaneously, but if it is a solid they must be carried out sequentially.

A vaporizable hydrocarbon feedstock (e.g., methane, propane, naphtha) is burned in a flame in the presence of about 35% of the stoichiometric amount of oxygen.



A little water is also formed by conventional combustion reactions. Excess hydrocarbon can now react.



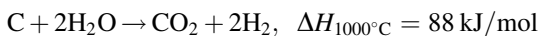
The flame temperature is 1300–1400°C at a pressure of 6–80 bar with a residence time of 2–5 seconds. The rapid initial reactions provide the heat required to drive the subsequent endothermic reactions. These reactions are slower than the initial reactions, however, and, because incomplete combustion is always accompanied by carbon formation, a finely divided carbon is always present in the products and must be removed by washing.

Desulfurization is unnecessary. Sulfur in the feedstock is converted primarily to hydrogen sulfide but also to carbonyl sulfide (COS). Nitrogen compounds end up as elemental nitrogen or ammonia. A plant must be built, however, to produce the pure oxygen for the process. This is generally an economic drawback but confers a slight advantage in ammonia manufacture, in that the nitrogen coproduced with the oxygen can be added to the synthesis gas to provide the correct composition for ammonia production. Some of the shift reaction and carbon dioxide removal stages can be avoided.

12.4.4 Solid Feedstocks

The two-stage, partial oxidation of coal has been widely used as a route to synthesis gas and the method could be extended to other carbonaceous feedstocks. A bed of coke or coal is burned in a stream of air until it reaches about 1000°C. The air is then

replaced by steam and two coal gasification reactions occur.



The product is called water gas because it is made from water plus coke. It is also called blue gas, because it burns with a characteristic blue flame caused by chemiluminescence (the $^3\text{B}_2$ bands of carbon dioxide). It can be converted to synthesis gas by techniques already described.

If air and steam are passed over the coke simultaneously, the product gases are diluted with nitrogen and are known as producer gas or low BTU gas. Producer gas is obsolete in the United States but is burned in situ as a cheap fuel gas in some parts of the world.

Much effort has been expended on the development of gasification processes for coal to produce synthesis gas for chemicals. Most important is the work done by Eastman, based on the Texaco gasifier, which led to a coal-based acetic anhydride process (Section 12.5.2.3).

12.4.5 Hydrogen

Hydrogen is manufactured by steam reforming and partial oxidation, but large amounts are also obtained in the refinery as by-products of cracking and catalytic reforming reactions (Sections 4.5 and 4.6). Minor sources include coke oven gases, as well as the electrolysis of aqueous sodium chloride (which gives principally sodium hydroxide and chlorine), as well as hydrogen chloride and hydrogen fluoride (to give chlorine and fluorine).

When hydrogen is obtained from synthesis gas or refinery processes, it is purified by washing successively at 180°C and about 20 bar with liquid methane, to remove nitrogen and carbon monoxide, and with liquid propane to remove methane.

About 60% of all hydrogen is used for the production of ammonia. The second largest use is in refinery processes in hydrotreating, hydrocracking (Section 4.11), hydrodesulfurization, and toluene hydrodealkylation (Section 10.1). Most of this hydrogen is produced internally in other refinery processes. The Clean Air Act, however, reduced permitted amounts of aromatic hydrocarbons in gasoline, hence less catalytic reforming is now done and less hydrogen is produced. Many refineries have experienced shortages and have found it necessary to build on-purpose hydrogen units. Among organic chemicals made outside the refinery, methanol is the largest consumer of hydrogen. Other applications include the conversion of benzene to cyclohexane (Section 9.2), nitrobenzene to aniline (Section 9.3), and unsaturated fats to saturated or hard fats (Chapter 15).

12.5 CHEMICALS FROM SYNTHESIS GAS

Forty-four percent of synthesis gas production is used for chemicals. The remainder is used for fuel and power applications and the production of Fisher–Tropsch liquids.

Ammonia is by far the most important chemical made from synthesis gas and consumes about 5% of the world's natural and associated gas production. Even though it is not organic, it is produced from and used to make organic chemicals. Methanol is the second important chemical from synthesis gas and is the basis for formaldehyde, acetic acid, and methyl *tert*-butyl ether (Section 7.2.1). It consumes about 1% of natural and associated gas production.

12.5.1 Ammonia and Its Derivatives

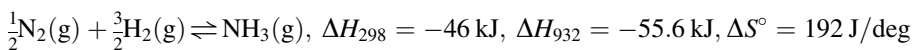
Chemically combined nitrogen in food and in our bodies is called “fixed” nitrogen. It is obtained either directly or indirectly from the soil, not from the air. Nitrogen consumed in food and not used for bodily protein is excreted, treated in sewage works, and ultimately carried out to sea. Human bodies are buried in the earth, but cemeteries are not cultivated for food; alternatively, the bodies are cremated, the “fixed” nitrogen reverting to elementary nitrogen. The soil's nitrogen content becomes depleted, and fertilizers are necessary.

12.5.1.1 The Crisis of Nitrogen Depletion

The first fertilizer to be exploited was guano, fossilized bird dung from the west coast of South America, but supplies ran out by the late 19th century. It was replaced by Chile saltpeter (sodium nitrate) from the waterless deserts of South America and supplemented by ammoniacal liquor from coke ovens. But there was a limit to that too. In 1898, Sir William Crookes, a distinguished scientist, predicted world starvation by about 1930 because of a famine of “fixed” nitrogen.

This disaster has been averted because Fritz Haber, a converted German Jew, discovered a way to react hydrogen with atmospheric nitrogen to make ammonia for conversion to sodium nitrate fertilizer and also to explosives. Announced in 1910, it was the most important chemical discovery of the twentieth century. Today, half the nitrogen atoms in everyone's body have resulted from the Haber process.

Haber realized from the thermodynamics of the reaction,



that the formation of ammonia would be favored by very high pressures (above 200 bar) and middling temperatures. Low temperatures would have led to an unacceptably slow reaction, high ones to a reduced yield. The compromise involved a catalyst, the initial one being impossibly expensive osmium, but iron was later found to be suitable.

The scale-up of Haber's idea was carried out by Carl Bosch (Nobel Laureate 1931) in the laboratories of Badische Anilin und Soda Fabrik (BASF). The high pressures were previously unattainable, and Bosch brought in armaments maker Krupp, whose gun barrels would withstand such conditions. Even so, the early pressure vessels exploded after a few days. This turned out to be due to the reaction of hydrogen with carbon in the steel. Bosch's solution was to line the vessels with soft carbon-free iron, which alone could not withstand the pressures but did protect the outer layer of steel.

In 1913, the first commercial factory came on stream and, in 1914, the First World War started. Imports of Chile saltpeter were blockaded. Without the Haber–Bosch process, Germany would have collapsed in 1915, so Haber’s discovery saved world agriculture, on one hand, but prolonged the war on the other. His subsequent pioneering of poison gas warfare harmed his reputation, but he was still awarded the chemistry Nobel Prize for 1918 for his great invention.

12.5.1.2 *Ammonia Manufacture*

The Haber–Bosch process requires a synthesis gas of composition $\text{N}_2:\text{H}_2 = 1:3$. The mixture is passed over a promoted iron oxide catalyst at about 450°C and 250 bar. Conversions are low, about 10% per pass, requiring a large recycle of unreacted synthesis gas.

Although the process is formally the same as that developed by Haber, the technology has been modified. More active catalysts have reduced the required operating temperature. The main change, however, has been the replacement of reciprocating pumps by centrifugal pumps. Reciprocating pumps operate like bicycle pumps with an in-and-out action and can achieve very high pressures. The earliest Haber plants were said to have operated at 1000 bar. Centrifugal pumps are like giant electric fans and involve only rotary motion. They are cheaper than reciprocating pumps, require less frequent maintenance, and do not require lubrication, so that oil contamination of the catalyst is avoided. They can be driven by turbines operated with the steam generated from waste heat or from the steam-reforming process. Their single drawback is that they are limited to pressures of about 250 bar. Their advantages, however, are so great that it is more economic to operate at this relatively low pressure and tolerate the low conversions.

This new technology has made possible the scaling-up of ammonia plants from the 200 metric tons/day, common in 1960, to 1500–1850 metric tons/day in the early 2000s. The first 3000 metric tons/day plant was commissioned in 2009 in Saudi Arabia. Steam crackers for ethylene also depend on centrifugal pumps, which have made possible impressive scale-up. Another development is the use of “skinned” microporous polysulfone membranes to separate unreacted hydrogen from the product stream so that it can be recycled without inert contaminants such as argon and without the waste involved in a purge stream (Section 9.1.2.3).

Iron-based catalysts have been used for so long that it seems almost heretical to suggest that they might be replaced. Meanwhile, the engineering company, Kellogg, Brown and Root, have proposed a ruthenium catalyst. At least one plant has been built (in Trinidad). It is said to enable the pressure to be reduced from 150–300 bar to 70–105 bar and the inlet–outlet temperature from $370\text{--}510^\circ\text{C}$ to $350\text{--}470^\circ\text{C}$. Waste heat is used for a synthesis gas reaction, and flue gas nitrogen oxides and carbon dioxide are reduced by 70–75% each.

It seems likely that the Haber–Bosch process will remain the mainstay of nitrogenous fertilizer production for the foreseeable future. There is still a hope for biological nitrogen fixation, whereby nonleguminous plants such as corn, wheat, and oats can be made nitrogen-fixing by bacteria created by genetic engineering techniques.

Should this objective be achieved, it might provide the basis for a second “Green Revolution” for food production which a rapidly increasing world population requires.

About 84% of ammonia production is used for fertilizers (Fig. 12.4) and the remainder as a feedstock for chemicals. The best way to apply nitrogen to the soil is by direct injection of ammonia, but the technology is complicated and is responsible for only 3% of consumption. By contrast, almost half of consumption is of urea, which is easy to ship and handle and contains 47% nitrogen. Ammonia reacts at about 190°C with carbon dioxide to give ammonium carbamate, which in turn dehydrates to urea.



The first reaction is rapid and exothermic (159 kJ/mol heat evolved) and the second stage is 29 kJ/mol endothermic, slow and equilibrium limited. Urea plants are always built next to ammonia plants, which supply the raw materials and also have excess heat available.

Urea was first synthesized by Wöhler in 1828, who heated an aqueous solution of ammonium cyanate at about 100°C.

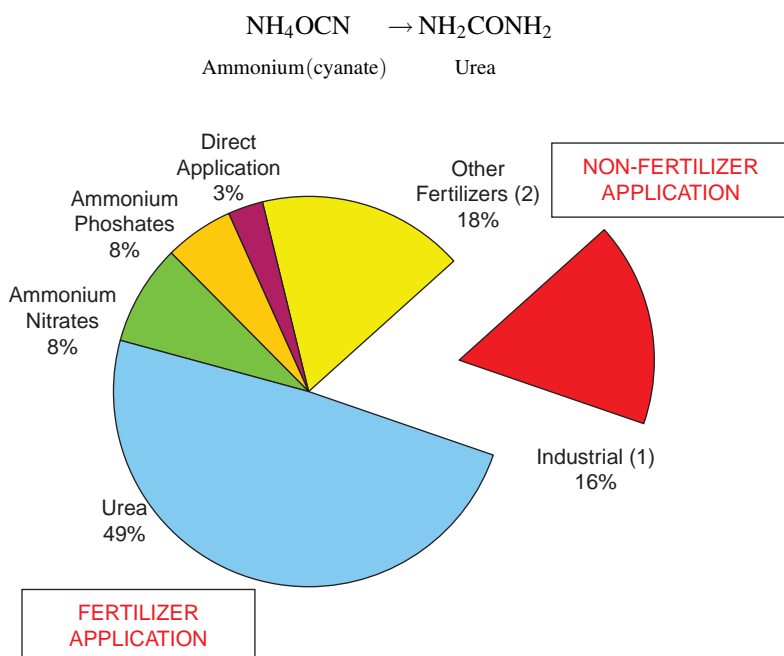
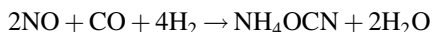


FIGURE 12.4 Global ammonia consumption, 2008 (160 million metric tons). (1) Industrial applications include the production of synthetic resins (e.g., urea-formaldehyde), synthetic fibers (e.g., acrylics and nylons), and explosives (e.g. ammonium nitrate). (2) “Other” fertilizers include ammonium sulfate, ammonium chloride, and compound nitrogen–phosphorus–potassium fertilizers. (Source: Nexant Inc.)

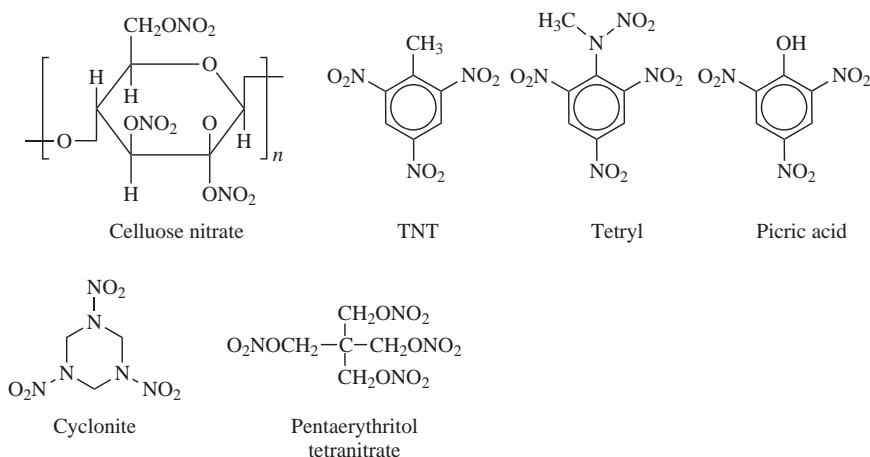
This seminal reaction, in which an inorganic compound was converted to an organic material, proved that organic chemicals, defined in those days as chemicals related to life, were chemicals like any other. The discovery gave rise to the discipline of organic chemistry. It had previously been thought that organic chemicals could only be made by living systems. Indeed, Wöhler defined an organic compound as one associated with life processes. Today the definition is much broader, for organic compounds are simply those that contain carbon.

Wöhler's reaction may have commercial application in that nitric oxide, carbon monoxide, and hydrogen have been found to combine at 60°C to give ammonium cyanate.



The reaction is catalyzed by a variety of metals including platinum and copper/nickel, although a platinum/rhodium gauze appears to be best. The ammonium cyanate in turn is converted quantitatively to urea, at 100°C. This reaction is not economically feasible as a route to urea because of the cost of NO, but it has been considered for removing emissions from automobile exhaust.

Ammonia may be oxidized to nitric acid, which is used, sometimes mixed with sulfuric acid, to produce a variety of nitro compounds and their derivatives. Most explosives [e.g., cellulose nitrate, TNT (trinitrotoluene), "Tetryl" (2,4,6-trinitrophenylmethylnitramide), picric acid (trinitrophenol), pentaerythritol tetranitrate, "Cyclonite" (cyclotrimethylene trinitramine), nitroglycerol, and ammonium nitrate] are nitro compounds, as are nitromethane, nitroethane, and the nitropropanes (Section 13.1), which are used as propellants, chemical intermediates, and solvents.



Nitrobenzene is the precursor of aniline and MDI (Sections 9.3.1). Dinitrotoluene is the precursor of toluene diisocyanate (Section 10.3). Nitrocyclohexane was an intermediate in an obsolete caprolactam process (Section 9.2.2) and the most

important caprolactam process uses ammonia-based hydroxylamine. Ammonia is important in ammoxidation (Section 6.5) and was involved in the first synthesis of hexamethylenediamine (Section 7.1.5). It is used similarly to convert fatty acids to amides (Section 15.2). It also reacts with alkyl halides, alcohols, and phenols to give amines (Section 9.3). Chemicals produced from ammonia, as noted above, are shown in Figure 12.4.

12.5.1.3 Urea and Melamine Resins

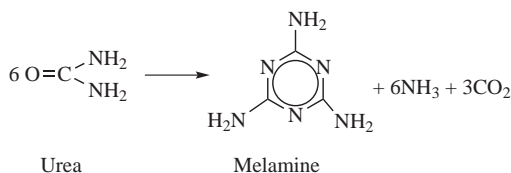
Urea reacts with formaldehyde to give thermosetting urea-formaldehyde (U/F) resins. The reactions are complex, involving first of all the formation of methylolurea and *N,N'*-dimethylolurea.



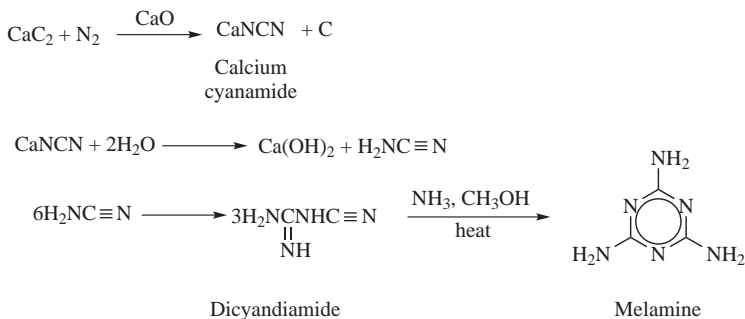
These, by a series of condensations that include ring formation, provide thermoset polymers (Section 17.4.1).

The major use for urea-formaldehyde (U/F) resins is as a binder for sawdust and wood particles in particle board. They are also used to creaseproof fabrics and to impart wet strength to paper. At one time they were used in the form of a foam as insulation for buildings, but this was discontinued because of a question about the toxicity of residual formaldehyde in such foams. Especially when the foam was new, traces of formaldehyde were given off, which presented a health hazard. Compression molding of urea-formaldehyde resins gives items such as electrical fittings and toilet seats. Molding powders are invariably formulated with fillers. They are less heat and water resistant than phenol-formaldehyde resins but can be fabricated in a range of cheerful colors. Curiously, 42% of European formaldehyde goes into amino resins, while the figure is only 24% in the United States.

Urea is also the source of melamine, which is made in the United States by a one-step process involving trimerization of molten urea at 400°C with release of ammonia and CO₂ in the presence of an aluminosilicate catalyst. Both low and high pressure processes are used and, in the former, cyanic acid, HNCO, is an intermediate.



An obsolescent process started with calcium carbide from coal and went by way of dicyandiamide. Some plants in Europe still use this process, and the global market for dicyandiamide was said to be 40,000 metric tons/year in 2002. Growth has not been great.



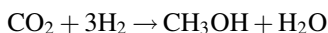
Like urea, melamine reacts with formaldehyde to give complex thermosetting resins. Melamine-formaldehyde (M/F) resins are high quality premium products and are used for dinnerware, the top layer of laminates such as “Formica,” and in industrial and decorative coatings, especially for automobiles. They make urethane foams fire retardant. Like the U/F resins, M/F resins are useful for textile and paper treatment, adhesives, and molding powders.

12.5.2 Methanol

Methanol is made from synthesis gas, most of which is derived from natural gas.¹⁰



Excess hydrogen is added for kinetic reasons although the CO:H₂ ratio may be as low as 1:2.02. The steam reforming of naphtha, which as indicated earlier is not widely used in the United States or Western Europe, produces synthesis gas close to the desired composition. The steam reforming of methane or natural gas yields a synthesis gas with a H₂:CO ratio close to 3:1. There are two ways of adjusting the ratio. The first is to purge the excess hydrogen, and the purged gas is normally burned as reformer fuel. The second is to add carbon dioxide from an external source such as an ammonia plant to take up the excess hydrogen although, as noted, a slight excess is maintained.



There is recent evidence that the mechanism of the reaction is one in which the carbon monoxide is converted by the shift reaction to carbon dioxide, after which the carbon dioxide reacts with hydrogen as shown above, to yield methanol. An uncommercialized process for methanol is based solely on carbon dioxide.¹¹

Initially methanol was prepared by BASF by a high pressure process (320–380°C and 340 bar) with a ZnO–Cr₂O₃ catalyst with Zn:Cr ratio of 70:30. In 1972 ICI commercialized a low pressure process (240–260°C and 50–100 bar) which made use of a copper zinc–catalyst on an alumina support. The energy savings are large but the process requires synthesis gas almost completely free of chlorine and sulfur compounds. There have since been a number of medium pressure processes (100–250 bar)

with copper oxide added to the Zn–Cr catalyst system. Techniques for purifying synthesis gas are sufficiently good to have made the ICI process dominant. Although the catalyst is more expensive, the reaction is more selective, giving higher methanol yields and purer product. The major side reaction is the formation of dimethyl ether from methanol. Aldehydes, ketones, esters and higher alcohols are formed in minute quantities. The methanol is refined by distillation.

At least four new processes are under development for methanol production, none of which has been commercialized. In one process, a homogeneous catalyst, typically ruthenium carbonyl, operates at temperatures as low as 120°C where the $\text{H}_2 + \text{CO}/\text{CH}_3\text{OH}$ equilibrium strongly favors methanol. Intermetallic catalysts have been explored extensively in a second process but thus far have not found commercial application. A barium–copper intermetallic compound makes possible methanol formation at 280°C and 60 bar. A zinc-promoted Raney-copper catalyst also has been shown to have higher activity than the Cu–Zn–alumina catalyst used in the standard low pressure process.

A liquid phase methanol process makes use of a copper–zinc catalyst supported on alumina. The reaction can take place at 250°C and 50 bar. The reaction is carried out in an inert liquid such as a hydrocarbon. Once the methanol forms, it is vaporized and purified. The process has been piloted jointly by Eastman Chemical and Air Products who operate a demonstration plant with the CO and H_2 prepared from coal. The possibility of producing methanol by direct oxidation of methane will be discussed in Section 13.1.1.

A new plant design has also attracted interest. BP/Kvaerner has developed a reformer consisting basically of a coaxial tube. A mixture of natural gas and steam is passed up the outer tube, which is filled with conventional steam reforming catalyst. The effluent from the top of the outer tube is then partially oxidized in a chamber with oxygen-containing gas before being passed down the inner tube, which is filled with secondary reforming catalyst. The energy released during the partial oxidation/secondary reforming stage in the inner tube is sufficient to drive the primary steam reforming stage in the outer tube. It is claimed that the reformer is lighter than a conventional unit, and is factory built, saving cost both at the fabricators and on-site. This example illustrates the importance attached to chemical engineering improvements in achieving marginal gains in the costing of large plants.

Various technology licensors are now developing “megamethanol” plants, with capacities on the order of 3000–5000 metric tons per day. Three plants produce more than 5000 metric tons per day, and each one represents about 5% of global demand. These huge plants are intended to maximize economies of scale and to allow methanol to be produced at remote locations from low cost “stranded” gas and still be cheap enough to tolerate shipping costs to developed markets.

Figure 12.5 shows both the growth of methanol capacity and the geographical shift. The most noticeable shift is from North America to Asia, but future growth is expected to be mainly in the Middle East. Plant closures in Europe and North America are expected.

Eighty-three percent of methanol produced in 2008 was used for chemicals (Fig. 12.6). The remaining 17% was used for fuels, particularly for the production

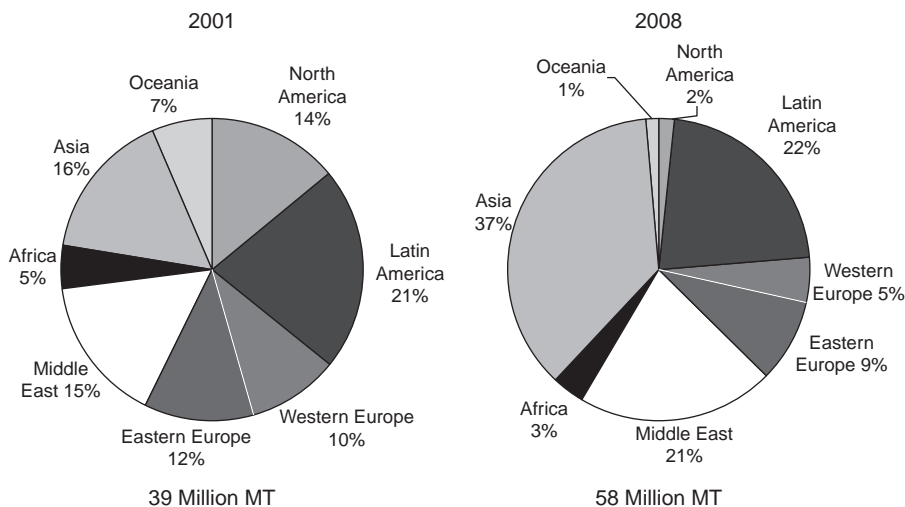


FIGURE 12.5 Capacity shift of methanol plants. (Source: Nexant Inc.)

of biodiesel and methyl *t*-butyl ether (Section 7.2.1). The sharp drop in MTBE usage has been compensated for by an increase in the use of methanol in biodiesel production, where it undergoes transesterification with triglycerides to give methyl esters of long chain fatty acids plus glycerol (Section 6.11.2). High oil prices have encouraged new uses such as fuel blending and dimethyl ether production in China, and methanol to gasoline and olefins (Sections 12.5.2.4 and 12.5.2.5).

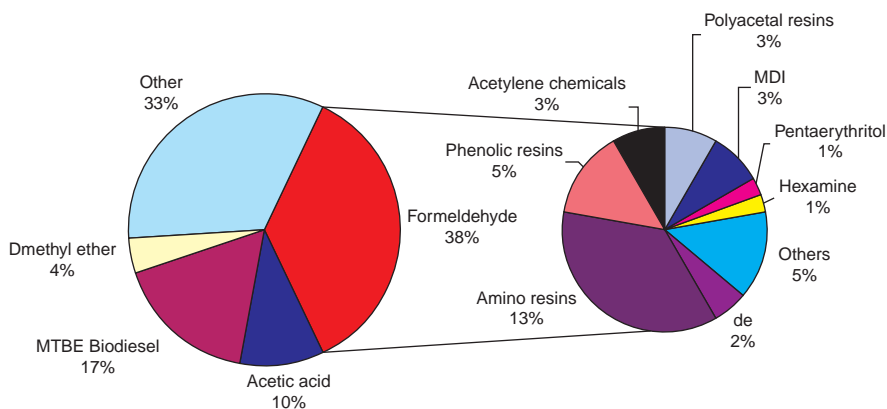


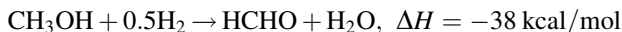
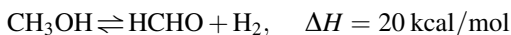
FIGURE 12.6 Global methanol and formaldehyde end-use patterns. Methanol, 44 million metric tons; formaldehyde, 28 million metric tons. The figures on the formaldehyde chart represent the percentage of methanol going into the specified end-use. To get the percentage of formaldehyde, multiply by 2.8.

Thirty-six percent of methanol is converted to formaldehyde. Apart from fuel applications, acetic acid and acetic anhydride (Sections 12.5.2.2 and 12.5.2.3) syntheses comprise the second largest use followed by methyl methacrylate (Section 6.7.1), terephthalic acid/dimethyl terephthalate (Section 11.3.3), methylamines, solvents, and a variety of lower volume chemicals including dimethyl sulfate and dimethyl carbonate (Section 9.1.2.2). These are not shown in the figure. Methanol is also used in the preparation of single cell protein (Section 16.6). Applications in the syntheses of chlorinated methanes (Section 12.2) and certain glycol ethers (Sections 5.11.6.2 and 6.8.2) are either banned or declining rapidly.

12.5.2.1 Formaldehyde

The major route to formaldehyde is the dehydrogenation/oxidation of methanol. Some producers use pure oxidation over a ferric oxide–molybdenum oxide catalyst. A small amount of formaldehyde is produced by the partial oxidation of lower petroleum hydrocarbons. Proposed methods include the hydrogenation of carbon monoxide, the pyrolysis of formates, and the direct oxidation of methane (Section 13.1).

The dehydrogenation/oxidation process uses a stationary bed silver catalyst and a mixture of methanol vapor and air at approximately atmospheric pressure and 700°C. Some water is added to facilitate methanol conversion and to prevent catalyst deactivation. Less than the stoichiometric amount of oxygen is used. The resulting gases are absorbed in water. It is believed that two gas phase reactions take place, one involving dehydrogenation and the other oxidation.



The first reaction, like all dehydrogenations, is endothermic and the second is exothermic. Properly carried out, a favorable heat balance results. There is some evidence that a second reaction does not in fact take place as written above, but rather that the exothermicity results from the oxidation of some of the methanol to CO_2 and water. Conversions as high as 75% have been reported with net molar yields of 83–92%. The by-product hydrogen plus traces of formaldehyde can be burned as fuel.

The oxidation process uses a ferric oxide–molybdenum oxide catalyst in a ratio of about 1:4. Reaction takes place at 300–400°C with almost quantitative methanol conversion at selectivities above 90%. Compared with the silver-catalyzed process, the lower temperature reduces corrosion problems, and higher formaldehyde concentrations are obtained without distillation. The drawbacks are that the great excess of air means higher capital and energy costs and, because the waste gas contains traces of formaldehyde, it is incombustible and must be specially purified. Consequently, most producers currently prefer silver catalysts.

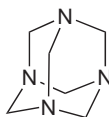
The gaseous formaldehyde is dissolved in water and, when prepared in this way, always contains 1–2% of methanol, which serves as a stabilizer. Commercial formaldehyde is sold in several forms. Aqueous solutions contain up to 60% formaldehyde

(37% is common) as a hydrate or as low molecular weight oxymethylene glycols $\text{H}[\text{OCH}_2]_n\text{OH}$. A second form is as a cyclic trimer called trioxane, and a third is “paraformaldehyde,” which forms when water is evaporated from an aqueous solution of formaldehyde. This polymeric form and the oxymethylene glycols are both readily “unzipped” by heat or acid.

Of the 28 million metric tons of formaldehyde produced worldwide in 2008, 13% was used for the preparation of phenol-formaldehyde resins (Section 9.1.1). Thirty-six percent was used for amino resins (Section 12.5.1.3), which, in the main, were urea-formaldehyde, but with a small contribution from melamine-formaldehyde resins (Fig. 12.6).

Polyacetal resins (Section 17.2) are polymers of formaldehyde with the recurring unit $-\text{OCH}_2-$. They are strong stiff polymers classified as “engineering” plastics, useful for replacing soft metals such as brass in, for example, valves, hose and tube connectors, as well as in hard metal uses such as machine housings and many structural parts.

A smaller use for formaldehyde is in the preparation of MDI/PMDI (Section 9.3.1). Formaldehyde combines with acetylene to give 1,4-butyndiol, which can be hydrogenated to 1,4-butanediol, and a series of related chemicals (Section 12.3.1). With ammonia it yields hexamine (hexamethylene tetramine or “Hexa”). Hexamine is an intermediate in the manufacture of RDX, the explosive that replaced TNT in “blockbuster” bombs in both World War II and the Korean War. Its principal use today is as a convenient source of formaldehyde under alkaline conditions for the curing of the B-stage or partially cured phenolic resins required in the manufacture of plywood or Formica.



Hexamine

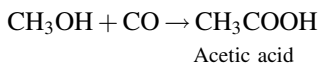
Formaldehyde with acetaldehyde yields pentaerythritol (Section 5.11.3). A related material, trimethylolpropane, is made by the condensation of formaldehyde and butyraldehyde (Section 6.9.1). Similarly, neopentyl glycol results from the condensation of formaldehyde and isobutyraldehyde (Section 6.9.1).

Nitrilotriacetic acid (Section 12.1) requires formaldehyde. One synthesis of isoprene depends on the condensation of formaldehyde and isobutene (Section 8.2). An uncommercialized process for ethylene glycol involves the dimerization of formaldehyde (Section 5.7.2).

12.5.2.2 Acetic Acid

Acetic (ethanoic) acid can be made by a number of routes, the oldest of which are the microbiological oxidation of ethanol to vinegar and the dry distillation of wood. The most important route today is Monsanto’s methanol carbonylation process, once

owned by BP but now transferred to INEOS together with the ethyl acetate from ethylene process (Section 5.9).



The reaction is catalyzed by iodine-promoted rhodium at 200°C. Pressure is 1–3 bar and selectivity is 99+% to acetic acid, based on methanol. This high selectivity is exceeded in industrial chemistry only by the reactions in which isobutene is reacted with water or methanol to give *t*-butanol or methyl *t*-butyl ether (Sections 7.2.1 and 7.2.4).

The Monsanto process followed on the heels of an older BASF process that used cobalt iodide CoI_2 as a catalyst. This synthesis, however, required a temperature of 250°C and a pressure of 60 bar and gave much lower selectivities than the Monsanto process. Numerous by-products complicated the purification of the acetic acid.

Both Celanese and BP have improved the Monsanto technology by enabling increased reactor throughputs.¹² The Celanese Acid Optimization (AO) process and the BP Cativa process have doubled or even trebled capacities with the need for only modest capital expenditure. The Cativa process uses an iridium-based catalyst in place of rhodium. The key to both Celanese's and BP's improved acetic acid technology is that the methanol carbonylation reaction is run in the presence of relatively low levels of water, about 4–5 wt %. This is in contrast to the conventional Monsanto process that requires about 14–15 wt %. The water is necessary to ensure that the rhodium catalyst remains in solution. Celanese discovered that adding lithium iodide to the reaction mixture stabilized the rhodium catalyst, while BP found that iridium-based catalysts were effective in a low water environment. Low water levels reduce energy consumption, decrease carbon monoxide unit consumption, increase reactor productivity, and lower unit capital investment.

Chiyoda in Japan has developed, and is offering for license, an acetic acid process that uses a heterogeneous methanol carbonylation catalyst, composed of rhodium complexed to a poly(vinylpyridine) resin.¹³

In the United States about 88% of all synthetic acetic acid is made by methanol carbonylation. The remainder is made via butane oxidation, except for a small amount formed as a by-product from poly(vinyl alcohol) and ethylene-vinyl alcohol copolymer production. In Western Europe, in the early 2000s, about 57% was made by methanol carbonylation, 28% by acetaldehyde oxidation, and 15% from light naphtha, but again methanol carbonylation is now the dominant method (see below).

On the order of 10% of world acetic acid is made by oxidative fermentation of ethanol from apple cider, wine, and fermented grain, malt, rice, or potato mashes with bacteria of the genus *Acetobacter*. In the submerged tank process, the ethanol is fermented to vinegar in a continuously stirred tank, and oxygen is supplied by bubbling air through the solution. Vinegar with 15% acetic acid can be prepared in only 24 hours. The method survives because many nations' food purity laws stipulate that vinegar used in foods must be of biological origin.

A method for making acetic acid, which was dominant in 1973 but is now virtually obsolete, is the oxidation of acetaldehyde made from ethylene (Section 5.5).

It involves treating a 5–15% acetaldehyde solution in acetic acid with air in the presence of dissolved cobalt or manganese acetates at 50–70°C. As indicated earlier, methanol carbonylation has been largely responsible for a decline in acetaldehyde production (Section 5.5).

In 1997 Showa Denko built a plant in Ōita, Japan, to oxidize ethylene directly to acetic acid via a palladium metal catalyst supported on a heteropoly acid such as tungstosilicic acid (Section 5.5). This process avoids the messy chemistry associated with the Wacker process for making acetaldehyde. It is thought to be competitive with methanol carbonylation for smaller plants (100–250 kt/a), depending on the local price of ethylene. In 2001, SABIC announced construction of a 30,000 metric ton per year plant for the selective catalytic oxidation of ethane to acetic acid.¹⁴ If successful, this technology would represent the second example of a commercially employed alkane activation technology, butane to maleic anhydride having been the first.

The second most important process in 1973 is also obsolescent. It is based on liquid oxidation of hydrocarbons – a crude butane fraction in the United States, and a light naphtha fraction called primary flash distillate in Europe, especially in the United Kingdom. The process requires large amounts of water and yields a dilute acetic acid solution whose concentration is energy intensive. The oxidation of butanes takes place at 175°C and 54 bar with a cobalt acetate catalyst. Many by-products are produced, the major one being methyl ethyl ketone. As late as 1982, 31% of U.S. acetic acid was made by this method. The oxidation of naphtha takes place at 70–90°C at 40 bar. As might be expected, even more by-products form than in the oxidation of butane. Important ones are propionic and formic acids and acetone. Succinic acid forms in substantial quantity but, in the early days, lacked a market and was burned along with the heavy ends. These hydrocarbon oxidation processes make use of the cheapest raw materials, but the separation of the acetic acid is complicated and expensive. Even so, the by-products have value in their own right and contributed to the economics of the process. Thus INEOS's UK plant at Hull did not close until the end of 2005.¹⁵ New plants to manufacture succinic acid by fermentation, starting with glucose and, remarkably, consuming carbon dioxide, are planned in Europe, one by INEOS at Hull and the other a joint venture between DSM and Roquette in the Netherlands.¹⁶ In the United States, BioAmber (Mineapolis) and Myriant (Quincy, MA) are planning a similar operation to start up in 2012.¹⁷ The market for succinic acid is 25,000–30,000 metric tons per year. It is used to make *N*-methylpyrrolidinone, 2-pyrrolidinone, succinate salts, γ -butyrolactone, and possibly 1,4-butanediol, maleic anhydride and tetrahydrofuran, although other routes look more attractive. The U.S. butane oxidation plants have continued to operate and presumably will do so until the fermentation route comes on stream.

Not yet commercialized are processes for making acetic acid by the direct combination of CO and hydrogen. One such process, pioneered by Texaco, makes use of a bimetallic ruthenium/cobalt system promoted by iodide. Selectivity, however, is far less than with the rhodium-catalyzed process.

Of the approximately 2.5 million metric tons of acetic acid consumed in the United States in 2008, over 51% is used for the preparation of vinyl acetate (Section 5.6). The end-use pattern is shown in Figure 12.7. A miscellany of commercial acetate esters

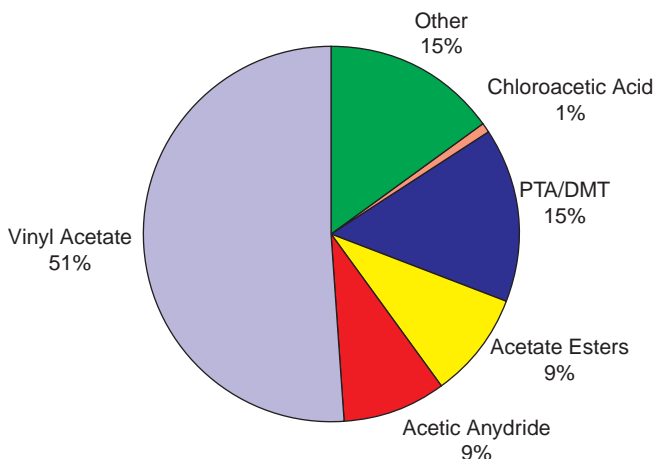
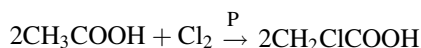


FIGURE 12.7 The U.S. synthetic acetic acid demand (2008). Consumption is approximately 2.5 million metric tons.

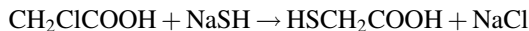
includes cellulose acetate (Section 16.4) and butyl, ethyl, *n*-propyl, and isopropyl acetates. However, the largest volume esters are acetates of glycol ethers (Section 5.11.6.2).

About 10% of acetic acid is also used as a solvent in the Amoco process for terephthalic acid (Section 11.3.1). Because much of it is oxidized, continual replacement is necessary. About 5% is converted to acetic anhydride.

Chloroacetic acid is made by direct chlorination of glacial acetic acid in the presence of red phosphorus:



About one-third of dichloroacetic acid production is converted to thioglycolic acid, a raw material for tin stabilizers for PVC;



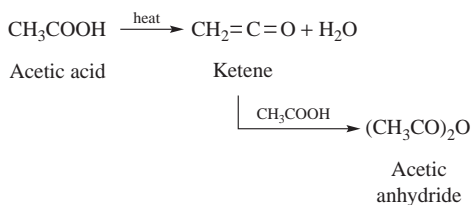
Another fifth is converted to carboxymethylcellulose (Section 16.4) and the remainder finds application in a number of small volume uses including conversion to glycine and to 2,4-dichlorophenoxyacetic acid, a common herbicide.¹⁸

Acetic acid is used in several textile operations including textile dyeing, and in the synthesis of photographic chemicals, rubber chemicals, pharmaceuticals, and herbicides. It is also used as a grain fumigant.

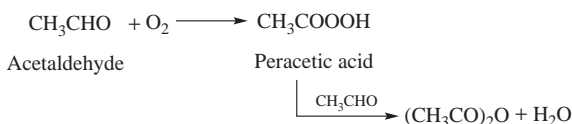
12.5.2.3 Acetic Anhydride

Acetic anhydride is made by three processes. In one, acetic acid (or acetone, but that is uneconomical) is pyrolyzed to ketene, which in turn reacts with acetic acid.

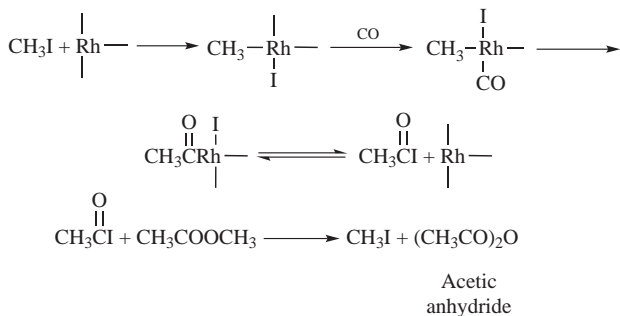
The pyrolysis takes place at 700–800°C in the presence of triethyl phosphate at a very low residence time of 0.2–0.5 second. Molar yields are 85–89%.



The second procedure involves the in situ production of peracetic acid from acetaldehyde, which in turn reacts with more acetaldehyde to yield the anhydride. This process is probably not in use. Ethyl acetate may be used as a solvent, and the reaction is catalyzed by a mixture of cobalt and copper acetates. The molar yield of acetic anhydride is about 75%.

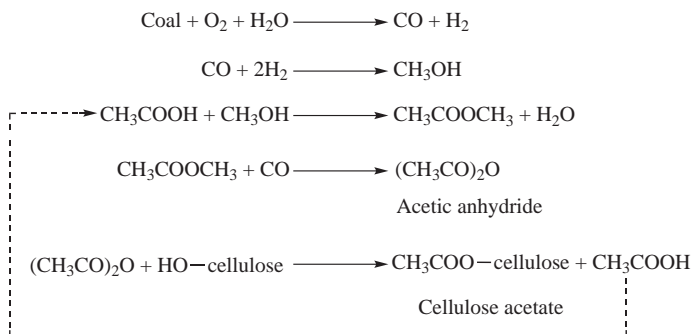


Eastman Chemical working with Halcon have developed a novel process involving the carbonylation of methyl acetate with a catalyst comprising rhodium chloride and chromium hexacarbonyl, $\text{Cr}(\text{CO})_6$, in an acetic acid solvent. In one reaction described in a patent,¹⁹ β -picoline is a catalyst modifier and methyl iodide is a promoter. The hydrogen/carbon monoxide ratio is important, since increase in the hydrogen content provides a corresponding increase in the production of ethylidene diacetate. This compound is the basis for a proposed process for vinyl acetate (Section 5.6) but is undesirable if high selectivity to the anhydride is desired. Since this reaction is novel, the possible mechanism is of interest. Only the rhodium is shown as the catalyst. In the first steps, acetyl iodide is formed. Reaction of this product with acetate ion yields acetic anhydride.



The Eastman/Halcon process is significant not only because of the imaginative chemistry involved but because the synthesis gas (Section 14.5) on which the process depends comes from coal. The Eastman plant in Tennessee is located close to the coal mines, which eliminates expensive transportation costs. The coal is gasified in an Eastman-modified Texaco gasifier operating at a high temperature to provide the synthesis gas with very little of the methane, which is undesirable for chemical operations. The acetic anhydride production is completely synthesis gas-based since the carbon monoxide and hydrogen react to form methanol. This in turn esterifies recovered acetic acid (see below) to provide the methyl acetate that is further carbonylated to acetic anhydride.

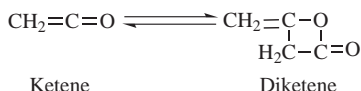
The acetic anhydride is used by Eastman for the esterification of cellulose to cellulose acetate (Section 16.4). In the process, a mole of acetic acid is released and is recycled, obviating the need for a dedicated acetic acid plant.



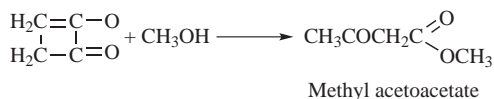
This is the only modern process in which coal has replaced petroleum. It provides confidence in the belief that coal can be used to manufacture all of the chemicals the world needs, should supplies of petroleum and natural gas be depleted. Full plant cost of the acetic anhydride produced by Eastman is 30% cheaper than the same product produced by conventional techniques. However, the investment for the coal-based process, because of the high cost of the gasifier, is roughly three times that of the investment for the conventional ketene-based process. Thus the use of coal requires a trade-off between high investment and low cost raw material. Also, the cost of coal-based chemicals will be increased because of the high cost of transporting coal.

Acetic anhydride's main use is in the production of cellulose acetate. Other uses are small and include the formation of various esters such as acetylsalicylic acid (aspirin) and acetylated amides of which *N*-acetyl-*p*-aminophenol (acetaminophen or paracetamol) is a prime example.

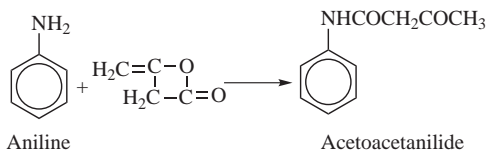
Ketene, the intermediate in one acetic anhydride process, is a powerfully lachrymatory gas with a choking smell. It is invariably used in situ. Apart from its role in acetic anhydride production, it can be dimerized over trimethyl phosphate to diketene. Ammonia is added to inhibit the back reaction.



Diketene reacts with methanol and ethanol to give methyl and ethyl acetoacetates.



It also reacts with aromatic amines to give acetoacetaryl amides. With aniline, acetoacetanilide is produced. This and its homologs are used in the production of azo dyes.



12.5.2.4 Methanol to Gasoline

In addition to the acetic anhydride process described above, there are several additional uses for methanol including conversion to gasoline and olefins, described below, and as a substrate for single cell protein, which is discussed in Section 16.6.

The process for converting methanol to gasoline, known as the Mobil MTG process, was operated in New Zealand from 1985 to 1995.^{20,21} It is a simple although high investment process. Like the Fischer–Tropsch process, it starts with the generation of synthesis gas. Methanol is generated by the ICI low pressure process (Section 12.5.2). The methanol is then brought into contact with a fixed bed of the acid form of the zeolite catalyst ZSM-5 (known as HZSM-5, see Section 18.9) at temperatures on the order of 380°C. There is a separation of carbon from oxygen, the former being polymerized into hydrocarbon chains and the latter emerging as water. The same reaction takes place over many acidic catalysts, but there is rapid coking and loss of catalytic activity. The geometrical selectivity of ZSM-5, however, does not allow for the formation of the linked aromatic rings that are the precursors of coke, hence the catalytic activity is maintained.

Water and CO₂ are the only oxygenated products of this highly exothermic reaction. To control the exotherm, the reaction is carried out in two stages. In the first, a dehydration catalyst such as CuO/γ-Al₂O₃ promotes methanol dehydration to dimethyl ether.

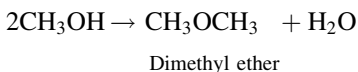


TABLE 12.3 Composition (mol %) of Gasoline from Methanol

	Reaction	Temperature
	370°C	538°C
C ₁ –C ₄ aliphatics	28.84	60.50
C ₅ + aliphatics	33.83	3.50
Benzene	0.96	
Toluene	4.69	
Xylenes	12.33	35.90
C ₉ aromatics	12.25	
C ₁₀ aromatics	7.10	
C ₁₁ + aromatics	—	0.10
Total aromatics	37.33	36.00

The resulting equilibrium mixture of methanol, water, and dimethyl ether is fed to the second reactor. The dimethyl ether appears to lose water, which diffuses easily out of the zeolite structure, to leave CH₂ radicals. The CH₂ radicals polymerize within the zeolite pore system to give alkanes and aromatic hydrocarbons up to the geometrical selectivity limit (C₁₀) imposed by the pore structure. A mixture of aliphatic and methylated aromatics results with a high octane number. Typical compositions at different temperatures are shown in Table 12.3. The major C₁₀ component is durene (2,3,5,6-tetramethylbenzene), a solid that must be removed. This MTG process without modification would not be suitable for the production of aromatics for the chemical industry unless catalyst changes increased benzene content appreciably.

In 2006, Uhde was awarded a contract by the Chinese company Shanxi Jincheng Anthracite Coal Mining for the engineering and supply of an MTG plant based on a proprietary zeolite-based process licensed from ExxonMobil. It is part of a complex on a pilot plant scale, which includes a fluidized-bed hard-coal gasification plant and a methanol plant. It came on stream in 2009 with an annual capacity of 100,000 metric tons of gasoline.

12.5.2.5 Methanol to Olefins

Mobil also found that its MTG catalyst could be modified to make light olefins from methanol but, as it was designed to make gasoline, it was not ideal. The relatively large pore size in ZSM-5 results in relatively low selectivity to ethylene and propylene. In the mid-1990s, UOP and Norsk Hydro developed a process and catalyst specifically to make light olefins (Table 12.4). Their MTO (methanol-to-olefins) process uses a silica aluminophosphate molecular sieve catalyst, SAPO-34.²² It is an acid material, some of the P⁵⁺ ions having been replaced by Si⁴⁺ and H⁺. It has a chabazite framework with a three-dimensional eight-membered ring system. The entry pores are 0.38 nm

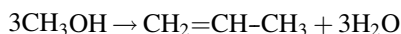
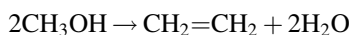
TABLE 12.4 Comparison of Light Olefin Production by Steam Cracking and Methanol-to-Olefins

	Steam Cracker	Steam Cracker	MTO	MTP
Catalyst	None	None	SAPO-34	Zeolite
Temperature (°C)	850–860	880–900	350–500	420–490
Feedstock	LVN	Ethane	Methanol	Methanol
<i>Mass balances: tonne/tonne of ethylene + propylene</i>				
Ethylene + propylene	1	1	1	1
Feedstock	1.9	1.2	3.0	3.1
Light products	0.39	0.20	0.07	0.02
C ₄ +	0.51	0	0.23	0.37
Water	0	0	1.7	1.75

Note: LVN = light virgin naphtha; SAPO = silicoaluminophosphate. In all cases except with the ethane cracker, the ethylene/propylene ratio can be varied somewhat by varying reaction temperatures and/or residence times.

across – narrower than ZSM-5, and equivalent to 3–4 atoms – and the cage size is 0.65 nm. The distribution of acidic sites is more controlled than in ZSM-5 and gives higher selectivity to ethylene and propylene. Unlike ZSM5, however, SAPO-34 is not physically robust and must be combined with special binders to enable it to withstand the rigors of fluidization. SAPO-34 gives about 78% selectivity to ethylene and propylene combined, on a total hydrocarbon basis. The relative amounts of ethylene and propylene can be altered to meet market demand to some degree by changing reactor severity.²³

Selectivities at 650 K are quoted as C₂–C₄ olefins 96%, methane 1.4%, ethane 0.3%, and propane 0.9%. The reaction proceeds via dimethyl ether and CH₂ radicals but the overall reactions may be written



One of the inherent problems of MTO technology is that, as a by-product of its conversion to CH₂ radicals, methanol loses a molecule of water. Thus 56% of the reactor output is water and 44% hydrocarbons. The plant must be large enough to cope with the aqueous flow, which increases its capital cost. In a conventional naphtha cracker, about 50% of the total output is ethylene and propylene, whereas in MTO only about 34% of the output is ethylene and propylene. Because of coking of the catalyst, the reaction is carried out in a fluidized bed with a second reactor to regenerate the catalyst, as in the plant for catalytic cracking (Section 4.6).

A variation of this approach is Lurgi's MTP (methanol-to-propylene) process. In MTP, a specially formulated zeolite catalyst is used to push the selectivity toward propylene production, which, on a percent carbon basis, is about 47% with only 4.6% ethylene. The remainder is 21% butenes, 15% heavier olefins, 8% paraffins,

1.7% naphthenes, and 2.8% aromatics. The economics of MTO processes are only viable if very low cost natural gas is secured. Total has built a pilot plant at Feluy in Belgium using UOP technology. It started up in July 2010 and was said to be working well. China Shenhua Coal to Liquids and Chemicals brought on stream in September 2010 the first commercial unit using Lurgi technology. It is intended to produce 600,000 metric tons of olefins from methanol.

The production of ethylene and propylene directly from feedstocks containing only a single carbon atom, and potentially from coal, without the problems inherent in the Fisher–Tropsch process, is such an achievement that it is worth saying something about the mechanism, even though there is continuing debate about it. It is an extraordinary example of the power of modern catalysis. If very pure methanol is used, no reaction occurs, and this is in any case practically unattainable. It requires organic reaction centers, which could arise from a feedstock impurity or be already present in the catalyst. These centers catalyze the reaction jointly with the active sites on the catalyst. This is in contrast to conventional catalysis, in which only the catalyst sites are active. Large molecules cannot gain access through the narrow pores so it is suggested that they arise from traces of acetone or perhaps ethanol. Acetone and ethanol have been suggested, and they are thought to oxidize to acetic acid which, in turn, reacts to give isobutene, which is too big to escape from the cage. Isobutene and possibly 2-butene rearrange and trimerize to give a heptamethylcyclopentenyl or possibly a heptamethylbenzenium cation (Fig. 12.8). Reaction is accompanied by an induction period and is autocatalytic. For example, the first traces of propylene to be formed can combine to give a C₁₂ ring compound.

The heptamethylbenzenium cation (**I**) loses a proton to the catalyst (**II**) and the exocyclic double bond reacts with methanol to give an ethyl group on the benzene ring (**III**). This may be lost to give a hexamethylbenzenium ion (**IV**) plus a molecule of ethylene, or it may lose a further proton and react with another methanol molecule to give an isopropyl group attached to the ring (**V**). The isopropyl group can then break away as propylene, leaving (**IV**); (**IV**) can donate a proton to the catalyst to restore hexamethylbenzene (**VI**) (see below). The essential intermediate in the cycle is the formation of two *gem*-methyl groups attached to the benzene ring. The more methyl branches that exist on the benzene ring, the more energetically favorable is the detachment of an alkene fragment.

Destruction of the catalyst in the laboratory and analysis of the contents of the “cages” shows the most abundant trapped material to be hexamethylbenzene. Tetra- and pentamethylbenzenes are also found together with hexamethylnaphthalene and (at long reaction times) polymethylphenanthrenes, which are coking precursors.

Under typical reaction temperatures (~650 K), thermodynamics predicts that the ratio of propylene to ethylene is between 5 and 10, but experimentally the ratio is observed to be between 0.5 and 1.

12.5.2.6 Lower Volume and Proposed Uses for Methanol

Lower volume uses for methanol include the production of methylamines, glycol ethers (Section 5.11.6.2), dimethyl sulfate, dimethyl carbonate, and methylated

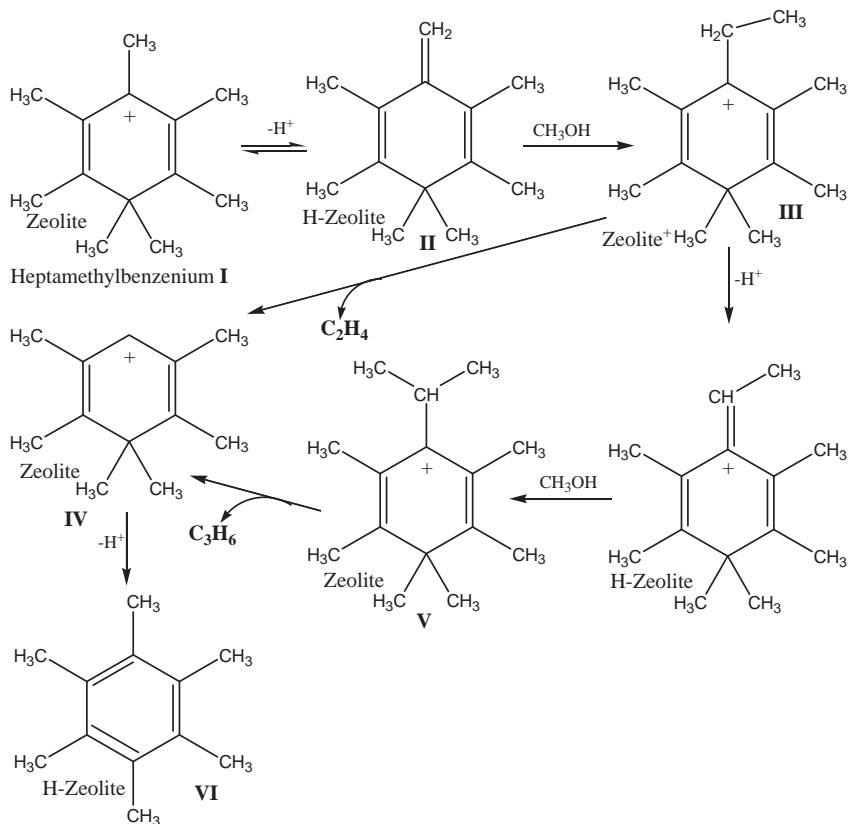
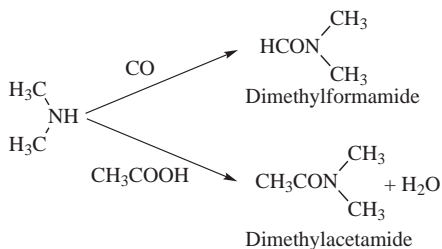


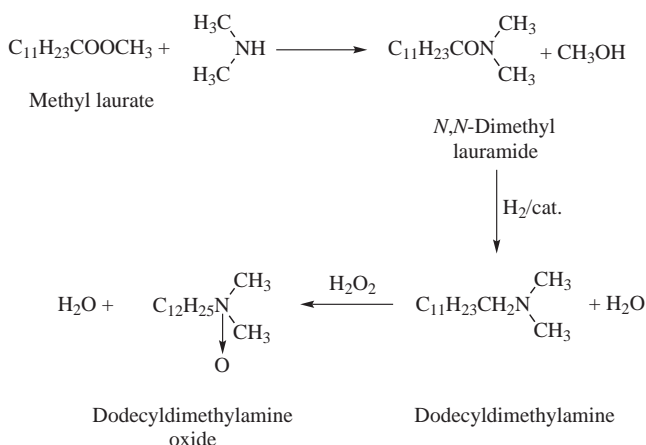
FIGURE 12.8 Formation of olefins from methanol over a SAPO-34 catalyst.

phenols. Methylamine, dimethylamine, and trimethylamine are made by the vapor phase ammonolysis of methanol at 450°C with an alumina gel catalyst. Conversion based on ammonia is 13.5% to primary, 7.5% to secondary, and 10.5% to tertiary amine. The separation of the three products is difficult. Trimethylamine can be separated from the mixture as an ammonia azeotrope. The mono- and diamines may be separated by fractionation. Another method of separation involves removing the dimethylamine, which is the most basic of the three, as the hydrochloride. Extractive distillation is also possible.

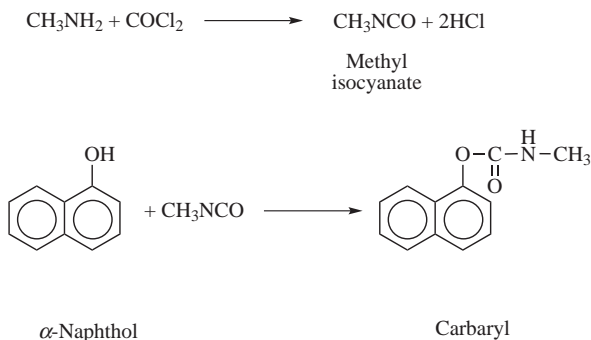
Dimethylamine is the product used in largest amount – about 270,000 metric tons was produced in 2005 – but is the smallest amount produced in the amination reaction. Thus the methylamine and trimethylamine are recycled without separation. Dimethylamine's largest uses are for conversion to dimethylformamide by carbonylation and to dimethylacetamide by reaction with acetic acid, acetic anhydride, or acetyl chloride. Both are solvents for the spinning of acrylic fibers and serve also as aprotic solvents for synthesis and extractive distillation.



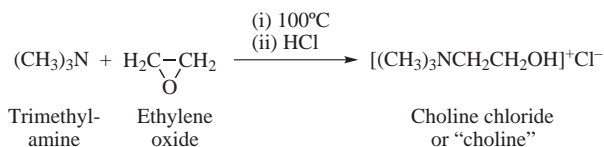
Other applications include the synthesis of dodecyldimethylamine oxide, a detergent ingredient, as shown in the following equations. It is also used for rubber chemicals such as thiuram accelerators, and for conversion to the dimethylamine salt of 2,4-dichlorophenoxyacetic acid, an important herbicide (Section 5.11.6.4).



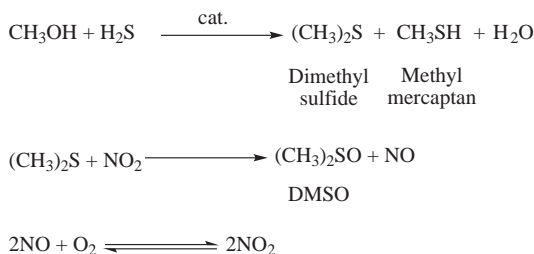
Methylamine and trimethylamine enjoy close to equal use of approximately 20,000 metric tons per year. A major application for methylamine is in the synthesis of the insecticide carbaryl. Methylamine reacts with phosgene to give the intermediate, methyl isocyanate the highly explosive chemical that gave rise to the Bhopal disaster. The methyl isocyanate then reacts with α -naphthol to yield carbaryl. An alternate process used by an Israeli company avoided the need for methyl isocyanate (Section 19.3).



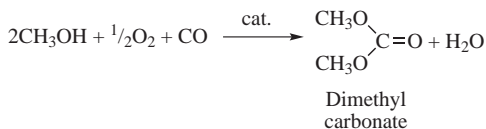
Trimethylamine's major use is in the synthesis of choline chloride, an important animal feed supplement, by reaction with ethylene oxide.



Dimethyl sulfoxide, an important aprotic solvent, is manufactured by the oxidation of dimethyl sulfide, which can be obtained either as a by-product from the Kraft paper pulping process or by the reaction of methanol with hydrogen sulfide, a reaction that also gives methyl mercaptan. The latter vapor phase reaction takes place at above 300°C and requires a dehydration catalyst. The oxidation to dimethyl sulfoxide can be carried out with nitrogen dioxide or, better, with oxygen containing a small amount of nitrogen dioxide. With the former, the reaction takes place at $40\text{--}50^\circ\text{C}$ and the product is purified by distillation.



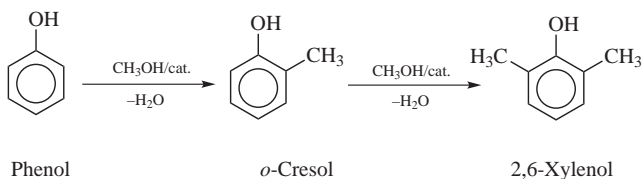
Dimethyl carbonate is made by the oxidative carbonylation of methanol with carbon monoxide and oxygen. These combine in the liquid phase in the presence of a copper-based catalyst to give dimethyl carbonate. The reaction can be carried out continuously at a pressure of about 25 bar with synthesis gas rather than pure CO, which is the only material consumed.



At conversions of 30–35% the yield of dimethyl carbonate is 100% based on methanol and 90–95% based on carbon monoxide. A newer process makes use of a solid copper methoxide with a nitrogen-containing cocatalyst capable of coordination, such as pyridine. Other approaches for making dimethyl carbonate are described in Section 9.1.2.2. Dimethyl carbonate is of current interest because it may be used for

alkylations in place of the more corrosive dimethyl sulfate, and because it can replace phosgene in the preparation of isocyanates and carbamates (Section 19.4). A General Electric patent describes a synthesis for polycarbonate resins that replaces phosgene with dimethyl carbonate (Section 9.1.2.2). General Electric has constructed two such plants in Japan and Spain. Dimethyl carbonate has also been suggested as an octane improver for gasoline.²⁴

Methanol is an alkylating agent. At 50 bar and a carefully controlled temperature of 300°C, it will alkylate phenol to *ortho*-cresol or to 2,6-xyleneol at about 50 bar over an alumina catalyst. Selectivity is high and only small amounts of ethers or *meta* or *para* alkylated products result. The ratio of *o*-cresol to 2,6-xyleneol can be varied by controlling pressure and temperature but these variations may promote the formation of by-products such as 2,4-xyleneol. The initial and insufficient source of *o*-cresol is coal tar distillate (Chapter 14). 2,6-Xyleneol is the monomer for an engineering polymer, poly(phenylene oxide).



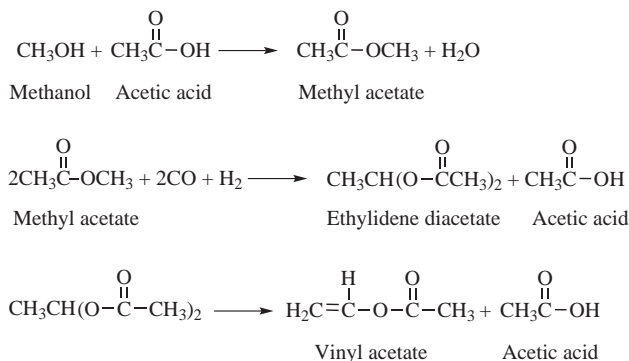
12.5.2.7 *C*₁-Based Development Processes

The elaborate chemistry of the olefin and aromatic feedstocks already described provides facile methods for obtaining and using organic compounds from C₂ upwards. The great divide is between C₁ compounds and those containing several carbon atoms, and much research has been focused on so-called C₁ chemistry since the 1970s.

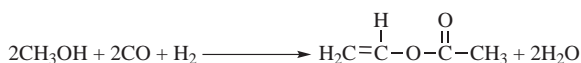
Meanwhile, C₁ chemistry has given rise to a number of processes that merit discussion. The chain reaction between methanol and formaldehyde to yield ethylene glycol was described in Section 5.7.2 and methanol's cracking to olefins in Section 12.5.2.5. Other reactions based on methanol include conversion to aromatics, synthesis of vinyl acetate via methyl acetate, and homologation to ethanol and higher alcohols.

Just as methanol may be cracked to olefins over one set of zeolite catalysts, it may be aromatized over others. One example has already been given for the MTG process (Section 12.5.2.4). The highly methylated aromatics are useful for gasoline but would have to be hydrodealkylated to give the benzene that the organic chemical industry needs. Further catalyst development is required.

Vinyl acetate (Section 5.6) can be prepared from methyl acetate by a process devised by Halcon reminiscent of the Eastman/Halcon acetic anhydride process (Section 12.5.2.3). Methyl acetate reacts with carbon monoxide and hydrogen to give ethylidene diacetate, which on pyrolysis provides vinyl acetate and acetic acid.



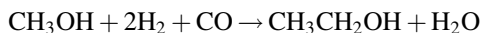
Since the acetic acid is recycled, the net reaction is



The carbonylation in the presence of hydrogen is accomplished with a rhodium chloride catalyst modified with β -picoline and promoted with methyl iodide. Acetic anhydride and acetaldehyde are obtained as by-products. The economics of the Halcon process seem reasonable although capital investment is considerably higher than for the conventional process.

The homologation of methanol to higher alcohols, which has never been commercialized, is nonetheless of interest as a route to ethanol whose price in 2010 was four times that of methanol. It also provides a route to higher alcohols, conceivably useful as oxygenates to augment octane numbers in unleaded gasoline.

The homologation of methanol to ethanol proceeds with a dicobalt octacarbonyl catalyst.



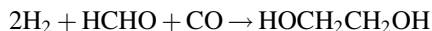
At 200 bar and 365°C, 76% conversion and a 40% selectivity to ethanol are obtained. A variety of other catalysts have been tested, including cobalt catalysts with phosphine ligands. A variant of the process involves the reaction of methanol with synthesis gas to give acetaldehyde, which can then be hydrogenated to ethanol. Typically, higher selectivities result when a reaction is carried out in two steps with the isolation of an intermediate. Many catalysts have been proposed for the preparation of acetaldehyde by this route, based on cobalt, nickel, palladium, ruthenium, and tungsten. In most instances, ligands are required.

The economics of these processes are attractive. Less favorable are the economics associated with either the homologation of methanol to alcohols higher than ethanol or to the production of higher alcohols from synthesis gas directly. Nonetheless, the high selectivity possible for obtaining specific alcohols from synthesis gas is demonstrated by work in which CO and hydrogen are combined to provide 44%

selectivity to isobutanol, whose dehydration to isobutene for conversion to methyl *t*-butyl ether was of interest earlier. The technology was not practiced because the reaction sequence *n*-butane \rightarrow isobutane \rightarrow isobutene is more economical (Section 7.2.1) and because methyl *t*-butyl ether is no longer in demand.

There are several methanol-based routes to ethylene glycol. Until 1968, DuPont produced ethylene glycol commercially from methanol, formaldehyde, and carbon dioxide. Formaldehyde is carbonylated to give glycolic acid in the presence of a strong acid (Section 5.7.2).

Esterification of the glycolic acid with methanol followed by hydrogenolysis of the ester also yields ethylene glycol (Section 5.7.2). The carbonylation takes place at 200°C and 70–100 bar at high selectivity, as does the esterification reaction. The hydrogenolysis occurs at 200°C and 30 bar with an appropriate catalyst. The released methanol is recycled so that the overall reaction is



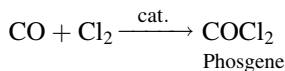
An improvement in this process involves the use of HF in the carbonylation step. The development of more active catalysts for the hydrogenolysis (Section 12.3) step, coupled with low cost synthesis gas from coal or stranded gas, could make the DuPont process feasible again.

12.6 CARBON MONOXIDE CHEMISTRY

Current industrial processes for C_1 production are based largely on methane (Sections 12.1–12.5) from natural gas. The other significant C_1 molecules comprise methanol, carbon monoxide, and formaldehyde. Interesting chemistry is in the wings based on these molecules, which are obtainable if necessary from coal.

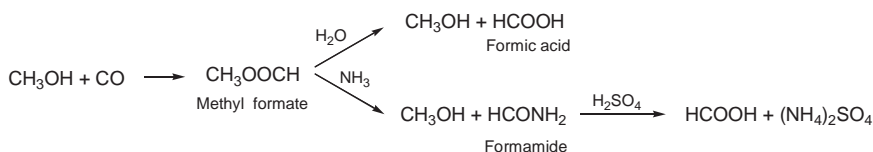
Carbon monoxide is the basic C_1 molecule. The largest application of C_1 chemistry is the production of methanol (Section 12.5.2). Striking examples of the replacement of classical chemistry by C_1 chemistry are the Monsanto acetic acid process (Section 12.5.2.2) and the Eastman acetic anhydride process (Section 12.5.2.3). The use of CO in hydroformylation has been discussed under propylene (Section 6.9.1). The use of CO for the preparation of dimethylformamide and dimethylacetamide was described in Section 12.5.2.6.

With chlorine, carbon monoxide yields phosgene. The reaction is carried out over activated charcoal at 250°C.

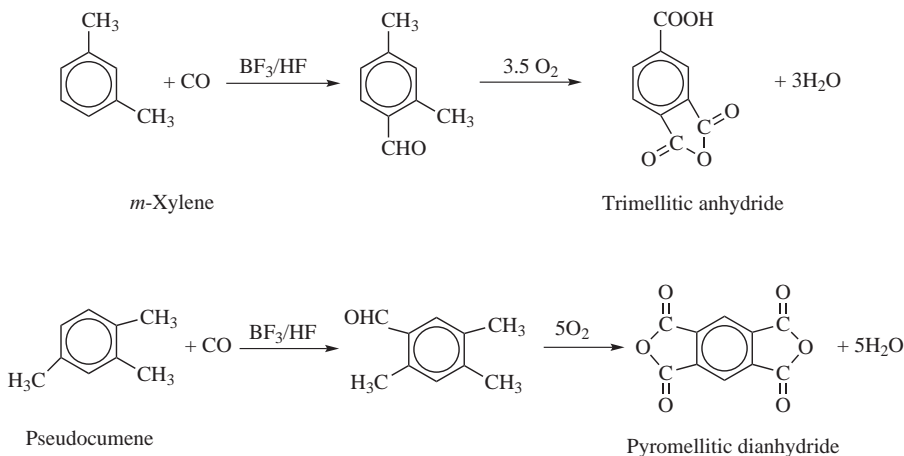


About 85% of U.S. phosgene is consumed in the production of diisocyanates (Section 9.3.1) and the bulk of the remainder for polycarbonate preparation (Section 9.1.2.2).

Formic acid is the simplest carboxylic acid. About 60% of global production is by the carbonylation of methanol to methyl formate followed by hydrolysis to formic acid and methanol, which is recycled. An alternative route is by ammonolysis of methyl formate to formamide followed by acidolysis with sulfuric acid to formic acid and ammonium sulfate. Formic acid is also a by-product in acetic acid production via butane or primary flash distillate oxidation (Section 12.5.2.2).



Mitsubishi Gas Chemical has developed a unique route for making precursors to trimellitic anhydride (TMA) and pyromellitic dianhydride (PMDA). The chemistry is based on the HF/BF_3 catalyzed addition of CO to *meta*-xylene and pseudocumene to give the corresponding dimethyl and trimethylbenzaldehydes. These are oxidized to TMA and PMDA.



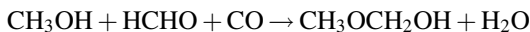
12.6.1 Proposed Chemistry Based on Carbon Monoxide

Proposed uses of carbon monoxide in industrial processes have been mentioned throughout this book. In particular, we have described the possibility of making ethylene glycol directly from CO and hydrogen (Section 5.7.2) and nonphosgene routes to isocyanates (Section 9.3.1). Much novel carbon monoxide chemistry is associated with glycols, glycol ethers, and glycol carbonates.

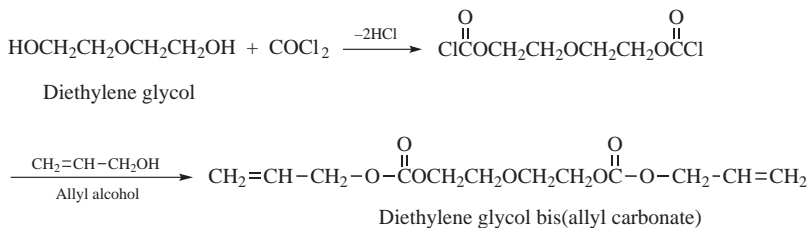
Union Carbide developed two processes that produced ethylene glycol directly from CO and hydrogen. One of the catalysts studied comprised a rhodium cluster with

operating conditions of 240°C and 1000–3500 bar. Reactions carried out under such severe conditions tend to have poor selectivity, and the economics of the Carbide process were harmed by the production of appreciable amounts of methanol. A two step approach involved condensing carbon monoxide and hydrogen with methanol to methyl oxalate followed by hydrolysis as in the DuPont process. Neither process was commercialized.

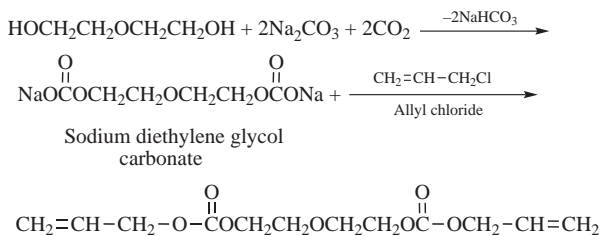
A proposed route to glycol ethers involves the combination of an alcohol with formaldehyde, carbon monoxide, and hydrogen. The reaction takes place at 180 bar and 160°C with a homogeneous catalyst comprising dicobalt octacarbonyl and donor ligands such as diphenyl sulfide and diphenyl oxide.



Diethylene glycol bis(allyl carbonate), also termed allyl diglycol carbonate, is a specialty polycarbonate polymer, whose major use is for molding eye glass lenses by in situ polymerization. A classical process involves the reaction of diethylene glycol with phosgene to give a bischloroformate, which, on further reaction with allyl alcohol, gives the desired product.



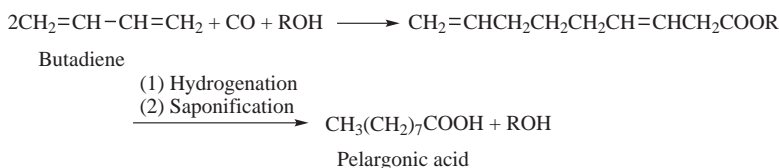
An alternative process operated on a pilot plant basis in Japan reacts diethylene glycol and allyl chloride with carbon dioxide in the presence of sodium carbonate. The reaction probably proceeds in two steps.



The idea of using carbon dioxide instead of phosgene could conceivably be expanded to the preparation of other carbonate polymers.

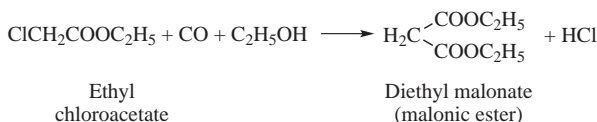
Carbon monoxide-based routes to pelargonic, malonic, phenylacetic, phenylpyruvic, and oxalic acids have been developed but mostly have not been commercialized. Currently there are two processes for pelargonic acid, one from natural sources (Section 15.7) and one based on 1-octene (Section 6.9.2) but it may also be made by

the dimerization of butadiene in the presence of carbon monoxide. The carbonylation is carried out homogeneously with carbon monoxide in alcohol in the presence of a palladium – phosphine complex. Hydrogenation and saponification provide pelargonic acid. Its major use is for synthetic lubricants.

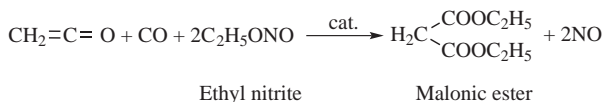


Palladium acetate or palladium acetylacetonate may be used as the source of palladium, with acetonitrile as solvent and methanol as the esterifying agent. The catalyst must be free of halide in order to effect dimerization of the butadiene. If halide is present, the butadiene is also carbonylated to give a 5-carbon unsaturated acid.

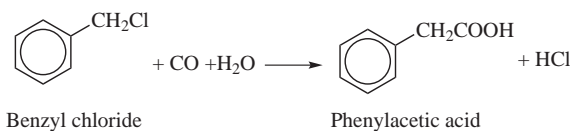
A malonic ester synthesis is based on the reaction of carbon monoxide, alcohol, and ethyl chloroacetate in the presence of cobalt tetracarbonyl at 55°C and 8 bar. The molar yield is 94%. The process is used in Germany and Japan. Global production of malonates is about 20,000 metric tons/year.²⁵



Another carbon monoxide-based process for malonic ester involves its interaction with ketene, and a nitrous acid ester. The reaction, which makes use of a platinum or platinum salt catalyst, proceeds at 115°C at atmospheric pressure but gives lower yields than the ethyl chloroacetate process.



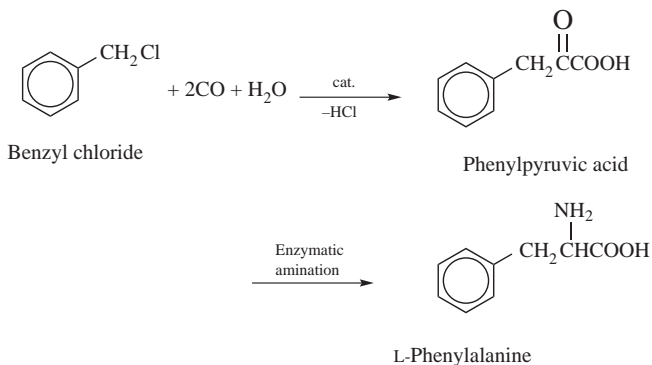
Phenylacetic acid results from the phase transfer carbonylation of benzyl chloride.



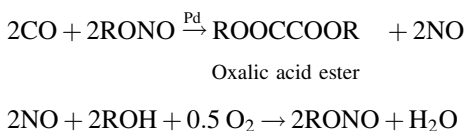
The aqueous phase comprises 40% aqueous sodium hydroxide solution. The organic phase contains a quaternary ammonium compound and a dicobalt octacarbonyl

catalyst. The quaternary ammonium salt transfers the cobalt carbonyl ion $[\text{Co}(\text{CO})_4]^-$ from the aqueous phase to the organic phase. The benzyl chloride, which is added continuously, is carbonylated under pressure.

Bis carbonylation of benzyl chloride gives phenylpyruvic acid. The reaction again requires a dicobalt octacarbonyl catalyst and proceeds in the presence of calcium hydroxide at 85°C and 60 bar in a *t*-butanol–water mixture. Phenylpyruvic acid is formed in a molar yield greater than 90%. Enzymatic amination of this compound yields L-phenylalanine, a key component of the noncaloric sweetener aspartame.



A Japanese process possibly in use for oxalic acid involves the oxidative coupling of carbon monoxide.



The reaction is carried out homogeneously at 110°C and 60 bar. In a corresponding heterogeneous reaction, palladium on carbon may be used at 120°C and atmospheric pressure. The oxalic acid ester on hydrogenolysis gives ethylene glycol. This process was mentioned earlier as an experimental one explored jointly by Union Carbide and UBE in Japan as a step in the proposed conversion of synthesis gas to ethylene glycol (Section 5.7.2).

α -Olefins (Section 5.3) result when synthesis gas is passed over a zeolite ZSM-5 catalyst impregnated with Fischer–Tropsch catalysts such as iron nitrate. The products have a chain-length distribution of 2–27 carbons but it is heavily skewed to the C_2 – C_5 compounds. It is noteworthy that both odd and even number carbon compounds result. Small concentrations of nonlinear olefins, alcohols, aldehydes, and ketones are also formed (Section 14.2). The process will require much more development before commercialization.

α -Olefins also are formed in the Fischer–Tropsch process as practiced in South Africa. Thus Sasol has become a dominant supplier of hexene-1 and octene-1, having developed extraction techniques for these products. Subsequently,

it devised processes for obtaining higher α -olefins, which are converted to detergent alcohols (Section 5.3.4).

12.7 GAS-TO-LIQUID FUELS

As described in Section 14.2, the Fischer–Tropsch reaction provides a means of converting synthesis gas to liquid hydrocarbons. This reaction was originally intended as a means to convert solid coal to liquid fuels but, in the mid-1990s and continuing into the 2000s, there has been growing recognition that the technology is also a means to convert and “monetize” low cost, “stranded” natural gas to liquid fuels.²⁶ Stranded gas is gas that has been discovered in remote areas such as southern Chile. Pipelines are the easiest way to transport gas but, the longer the pipeline, the more it costs, and eventually it becomes uneconomic. Liquefied natural gas (LNG) is another alternative but this method is also capital intensive.²⁷ Hence the interest in converting stranded gas to carbon monoxide and hydrogen at the point of origin and then to transportable liquid fuel by the Fischer–Tropsch reaction. Large companies such as Sasol, ExxonMobil, Conoco, and Shell have developed gas-to-liquid (GTL) process technology. Small entrepreneurial companies such as Rentech and Syntroleum have also developed niche technologies.

12.7.1 Sasol GTL Technology

Sasol’s application of Fischer–Tropsch technology dates back to the mid-1950s. Their original plant in Secunda, South Africa, employed a fixed bed reactor and produced 8000 barrels per day of liquid fuels from coal. In 1991, Sasol commercialized what has been called the world’s largest synthetic fuel project. This plant, located in Mossel Bay, South Africa, converts not coal but natural gas to gasoline using Sasol’s proprietary circulating fluidized bed reactor (Synthol). Sasol’s newest synthetic fuels technology uses a new slurry bed reactor. Its design has been simplified; it is easier to fabricate and is less expensive. The reactor consists of a shell with cooling coils in which steam is generated to remove the heat of reaction. Synthesis gas is distributed in the bottom of the reactor and rises through the slurry, which consists of reaction products, predominantly wax. The iron-based catalyst particles are suspended in the slurry. Because of the interaction between the slurry and the gas bubbles, the reactor contents are well mixed, permitting accurate temperature control. Sasol is involved in two major projects, one in Qatar and another in Nigeria, where the slurry phase technology will be used to convert gas to liquid fuels.

12.7.2 Shell Middle Distillate Synthesis

The Shell Middle Distillate Synthesis is an example of GTL technology and it is practiced in Malaysia with indigenous gas. It can also be used with associated gas, and a project was underway in Nigeria in the early 2000s to do this, partly to avoid the pollution caused by flaring. Unlike other Fischer–Tropsch technologies that are geared

to produce diesel fuel (Section 4.1), SMDS is designed to maximize middle distillates (boiling range 180–400°C), which contain diesel fuel as well as aviation kerosene.

Shell, as indicated above, built a 12,000 barrel per day SMDS plant in Bintulu, Malaysia, in 1993. The SMDS process produces synthesis gas from natural gas via noncatalytic partial oxidation (POX). Shell uses a tubular fixed Fischer–Tropsch reactor with a zirconium-promoted cobalt catalyst system that is intended to produce high selectivity to paraffin waxes. Wax production is high even in the normal reaction (see Table 12.4). Conversion is in excess of 80% in order to maximize the formation of the heavy paraffins or waxes. These waxes are subsequently hydrocracked (Section 4.11) to give a maximum yield of diesel fuel along with some naphtha and kerosene. In addition, a solvent fraction and hydrocarbons for detergent feedstock are produced. These are dehydrogenated to olefins for alkylation of benzene. The alkylbenzenes are sulfonated to give detergent intermediates (Section 9.4).

12.7.3 Other GTL Technologies

ExxonMobil has a large patent portfolio of gas conversion technologies. This research has led to ExxonMobil's Advanced Gas Concept 21st Century (AGC-21) process. It is a three-step process consisting of a fluid bed POX synthesis gas reactor, a slurry phase Fischer–Tropsch reactor, and a fixed bed hydroisomerization unit for product upgrading. This process has not yet been commercialized.

Syntroleum of Tulsa, Oklahoma, has developed a gas-to-liquid fuels technology called the Syntroleum process.²⁸ Its major innovation is the use of air instead of oxygen in the partial oxidation synthesis gas reaction. In traditional synthesis gas reactors, high gas conversion is achieved by a recycle loop; oxygen is used instead of air in order to avoid a build-up of nitrogen gas in the recycle loop. In the Syntroleum process, a cascade of one-pass reactors is used to achieve high gas conversions and, because there is no recycling, the nitrogen contained in the air is not a problem. The nitrogen gas also serves as an effective heat transfer agent. One of the most capital intensive steps in synthetic fuels production is the air separation unit for oxygen production. Since the Syntroleum process obviates this step, Syntroleum claims that synfuel production can be economic on a relatively small scale.

ConocoPhillips also has developed a gas-to-liquid fuels process. The synthesis gas technology is based on a low cost compact partial oxidation, while the Fischer–Tropsch technology is based on a proprietary cobalt catalyst that produces a high proportion of diesel fuel and naphtha. Heavier products are hydrocracked. Another gas-to-liquid fuels technology has been developed by Rentech. The Rentech process is designed to work with all gasification technologies. The Fischer–Tropsch reactor is a slurry bubble design used in conjunction with a proprietary iron-based synthesis catalyst.

ENDNOTES

1. The World Bank, World Bank, *GGFR Partners Unlock Value of Wasted Gas*, www.worldbank.org.

2. We thank Victoria Cook of the Imperial War Museum, London, for the information about Zyklon B. It is difficult to estimate the exact numbers murdered by hydrogen cyanide, and, for further details, we were referred to *Nazi Mass Murder: A Documentary History of the Use of Poison Gas*, eds. E. Kogon, H. Langbein, and A. Ruckerl, Yale University Press, New Haven, 1993.
3. In this section we use the systematic rather than the trivial names for the chloromethanes. Thus we use chloromethane for methyl chloride, dichloromethane for methylene chloride, trichloromethane for chloroform, and tetrachloromethane for carbon tetrachloride. The technical literature is less consistent and cheerfully mixes terms such as dichloromethane with chloroform.
4. D. Reay and C. M. Hogan, *Greenhouse Gas*, eds. H. Hanson, M. L. Pidwirny, and C. J. Cleveland, *Encyclopedia of Earth*. National Council for Science and the Environment. Washington DC, 2011.
5. G. W. Gribble, The diversity of naturally occurring organobromine compounds, *Chem. Soc. Rev.*, **28**, 335–346, 1999.
6. Nexant ChemSystems special report, *Chemicals from Acetylene. Back to the Future?* July 2007.
7. Nexant ChemSystems PERP report 98/99S1, *1,4-Butanediol/THF* (August 1998) provides detailed descriptions of routes and economics of 1,4-butanediol and THF.
8. <http://www.epa.gov/greenchemistry/pubs/pgcc/winners/gspall.html>.
9. *Chem. Eng. News*, 29 November 2010, p. 24.
10. Nexant ChemSystems PERP report 98/99-4, *Methanol* (May 2000).
11. J. Haggin, *Chem. Eng. News*, 28, March 1994, p. 29; D. Rotman, *Chem. Week*, 23 March 1994, p. 14.
12. A comparison of the conventional Monsanto acetic acid process with the Celanese acid optimization process is given by M. Gauss et al., *Appl. Homogen. Catal. Organ. Compd.*, **1**, 104–138, 1996.
13. For Chiyoda's acetic acid process see U.S. Patents 5,334,755 (2 August 1994) and 5,364,963 (15 November 1994) both to Chiyoda.
14. K. Sano, H. Uchida, and S. Wakabayashi. A new process for acetic acid production by direct oxidation of ethylene. *Catalysis Surveys from Asia*, **3**, 55–60, 1999. doi:10.1023/A:1019003230537; SABIC's technology for converting ethane directly to acetic acid is described in U.S. Patents 6,087,297 (11 July 2000), 6,060,421 (9 May 2000), 6,030,920 (29 February 2000), 6,028,221 (22 February 2000), 6,013,597 (11 January 2000), and 5,907,056 (25 May 1999) all to Saudi Basic Industries Corporation.
15. <http://media.rice.edu/images/media/Dateline/SpecialtyChemicalsMagazine0609.pdf>. Dr. Malcolm Joslin, BP, Saltend, (01482) 892513, personal communication.
16. *Chem. & Eng. News*, 22 December 2009.
17. *Chem. Week*, 17/24 January 2011, p.11.
18. *Chem. Market Reporter*, 19 May 2003.
19. The Eastman/Halcon process for acetic anhydride is described in West German Patents 2610035 (3 October 1976) and 2610036 (23 September 1976) both to Halcon.
20. <http://nzic.org.nz/ChemProcesses/energy/7D.pdf>.

21. http://www.exxonmobil.com/Apps/RefiningTechnologies/files/sell-sheet_09_mtg_brochure.pdf.
22. For UOP's MTO technology, see U.S. Patents 5,714,662 (3 February 1998), 5,774,680 (28 April 1998), 5,817,906 (6 October 1998), and 6,049,017 (11 April 2000) all to UOP. Another process claiming high selectivity to propylene by methanol cracking is described in European Patent Application 0105591 (8 April 1984) to Mobil Oil. Lurgi's Methanol to Propylene process is described in European Patents 0 882 692 A1 (9 December 1998) to Metallgesellschaft AG and 0 448 000 B1 (25 May 1994 to Sud-Chemie AG and Metallgesellschaft AG and U.S. Patent 5,981,819 (9 November 1999) to Metallgesellschaft AG.
23. For the mechanism of SAPO-34 MTO catalysis, see http://www.fhi-berlin.mpg.de/acnew/departement/pages/teaching/pages/teaching__wintersemester__2007_2008/bare_mto_301107.pdf; you may have to go as far as "department" and navigate from there, but it's worth it.
24. P. Tundo and M. Selva, The chemistry of dimethyl carbonate, *Acc. Chem. Res.*, **35** (9), 706–16, 2002.
25. <http://www.inchem.org/documents/sids/sids/malonates.pdf>.
26. See Nexant ChemSystems' multiclient report, *Stranded Gas Utilization* (January 2001).
27. The potential economic impact of low cost stranded gas on various C₁-based process technologies is discussed in Nexant ChemSystems PERP report 99/00S9, *Extending the Methane Value Chain* (October 2000).
28. Syntroleum's GTL technology is described in U.S. Patent 6,172,124 (9 January 2001). Rentech's GTL technology is described in U.S. Patent 6,534,552 (18 March 2003).

CHAPTER 13

Chemicals from Alkanes

Alkanes occur as such in natural gas and petroleum, and accordingly are the cheapest raw materials for chemicals. They are the feedstocks for cracking (Sections 4.5 and 4.6) and catalytic reforming (Section 4.8). Methane is the main source for synthesis gas (Section 12.4.1) via steam reforming. The higher alkanes can be subjected to the same process if desired, or the steam reforming process can be redirected to give methane. An important process is pyrolysis of hydrocarbons to carbon black, which is discussed at the end of this chapter.

Apart from pyrolysis, these reactions are endothermic and accompanied by an increase of entropy. They are all unselective and take place at high temperatures. There are few long-established examples of alkane functionalization, that is, of the use of alkanes directly for downstream chemicals. The most important are the conversion of *n*-butane to maleic anhydride (Section 7.4.2), the oxidation of *n*-butane or naphtha to acetic acid (Section 12.5.2.2), the oxidation of isobutane to *t*-butylhydroperoxide (Section 6.8), the oxidation of ethylbenzene to ethylbenzene hydroperoxide (Section 6.8), and the chlorination of methane (Section 12.2). Lesser volume uses involve ammoxidation of methane to hydrocyanic acid (Section 12.1), conversion of methane to acetylene (Section 12.3), and nitration of propane. These have largely been discussed.

Any alkane may be nitrated. In practice only propane is used as feed, and from its nitration result nitromethane, nitroethane, and 1- and 2-nitropropane. The nitration takes place at 420°C, and the products are separated by distillation. They are used as additives for gasoline for racing cars, as solvents especially for polycyanoacrylates, and as stabilizers of chlorinated solvents. DuPont developed a process for the nitration of cyclohexane to nitrocyclohexane as a step in a caprolactam synthesis (Section 9.2.2) but it is not currently used.

In the early 1990s a propylene shortage, primarily in Europe, motivated development of processes for the dehydrogenation of propane (Section 4.12). *n*-Butane also may be dehydrogenated to butadiene (Chapter 7) but it is more energy efficient to use *n*-butenes. The dehydrogenation of ethane to ethylene (Section 13.2.2) has not been commercialized. Important in the 1990s was the dehydrogenation of isobutane to

isobutene for methyl *tert*-butyl ether (MTBE)(Section 7.2.1), but the need for this has diminished.

The functionalization of alkanes is a research goal not only because of the economic advantage of circumventing the cracking process but also because reserves of methane – and to a lesser extent ethane, propane, and *n*-butane from natural or associated gas – may last longer than those of petroleum. The current route to chemicals from methane is via synthesis gas (Section 12.4) but the reaction is capital and energy intensive. Hence the objective is to functionalize methane by a direct process.

The strong and equivalent C–H bonds in methane make “bond activation” difficult. Thus the functionalization of methane is a “holy grail” for the chemist. If it can be successfully accomplished, the reward is great, because the chemical industry will have the lowest cost raw material possible. Progress to this goal has been made by the development of molecular sieve technology. It is admittedly a roundabout route, but methane will readily give methanol, which, when trapped in sieve cavities, loses water and gives a “soup” of CH₂ radicals capable of recombining in various ways. These are discussed in Sections 12.5.2.4 and 12.5.2.5.

13.1 FUNCTIONALIZATION OF METHANE

Early research on the functionalization of methane suggested that chemistry would never be discovered to make it the chemical industry’s basic building block. The advances in catalysis in the 1980s, however, motivated intense research on methane functionalization. And this accelerated in the 1990s. In the 2000s, however, it became clear that methane functionalization was an elusive target, and molecular sieve technology was the only promising approach.

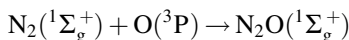
Three reactions provide the goals. These are the direct oxidation of methane to methanol and/or formaldehyde; the dimerization of methane to ethane, ethylene, or higher hydrocarbons; and the aromatization of methane.

13.1.1 Methane to Methanol/Formaldehyde

The oxidation of methane to methanol and formaldehyde is burdened by the fact that formaldehyde is 21 times more susceptible to oxidation than methane at 670°C. Methanol is even more sensitive to oxidation. Of the scores of patents issued, one to Hüls is typical. Methane and oxygen are mixed at 300–600°C at a pressure of 400 bar. Residence time is a critical 10^{−3} second. Conversions per pass, however, are no greater than 3%. The process is not currently economical because of the high capital investment that the short residence time and the low conversion rates necessitate. These negative factors provide the incentives for further research.

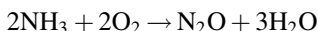
Nitrous oxide appears to be a particularly good oxidant for methane, and two Japanese patents¹ claim its use with catalysts such as Mo₃/SiO₂ and V₂O₅ at 450–550°C. A 93% selectivity to formaldehyde was obtained but at a conversion of only 0.5%. At 11% conversion, a 98% selectivity was achieved to a mixture of methanol and formaldehyde. At this latter conversion, the process shows some

promise, but its practicality is questionable because the molar ratio of nitrous oxide to methane must be 2:1. Nitrous oxide has historically been an expensive oxidant, because it could not be made directly from nitrogen and oxygen and required a roundabout route via ammonium nitrate. Oxygen atoms do not interact with nitrogen because the process,



is spin forbidden. That is, the nitrogen molecule has no unpaired electrons, and oxygen atoms have two, hence the total electron spin of the products should be two, not zero as in nitrous oxide. The reaction to give two molecules of NO, each of which has one unpaired electron, is far more likely.

In the mid-1990s Mitsui Toatsu developed a route to nitrous oxide via catalytic reaction of oxygen and ammonia.² The Mitsui Toatsu catalyst is a copper–manganese oxide (CuO–MnO₂)



Solutia has tried to lower the costs of this route even further by replacing the oxygen with air. Ammonia is still more expensive than nitrogen but not nearly as expensive as ammonium nitrate. Industrial oxidations of alkanes or aromatics with nitrous oxide may become practical in the future.

Typical of more recent work is a Catalytica process in which methane reacts with sulfuric acid to yield methyl hydrogen sulfate, CH₃OSO₃H, which can easily be hydrolyzed to methanol and recoverable sulfuric acid. The original catalyst was based on mercury, which would cause environmental concerns if used in a large scale process. Catalytica was able to replace this with a platinum complex^{3,4} (Fig. 13.1). At 180°C, selectivity to methanol was 86%. Catalytica spent five years and over \$10 million to develop the catalyst, but its process proved too costly and there were ongoing problems with reaction rate and yield.⁵

In 2008, Dow Chemical put up over \$6.4 million for methane activation research led by teams at Northwestern University and the UK's Cardiff University, but no breakthroughs have yet been reported.

A catalyst company, Siluria, is tackling the problem by growing catalyst crystals on the surface of a virus.^{6,7} Their virus is 900 nanometers long and 9 nanometers in diameter and serves as a template for the formation of equally small nanowires when it is exposed to metals and other elements under the right conditions. By genetically engineering the virus, a huge number of amino acid combinations appear on its surface. A metal is added to the catalyst by combining the virus with a metal oxide such as magnesium oxide that crystallizes out with the amino acid combinations. These structures are then screened and, apparently, some have been found that will bring about the oxidative coupling of methane to give ethylene.

C–H activation is a topic of great interest to the research community, but progress is slow. The situation is reviewed briefly by E. Davies.⁵

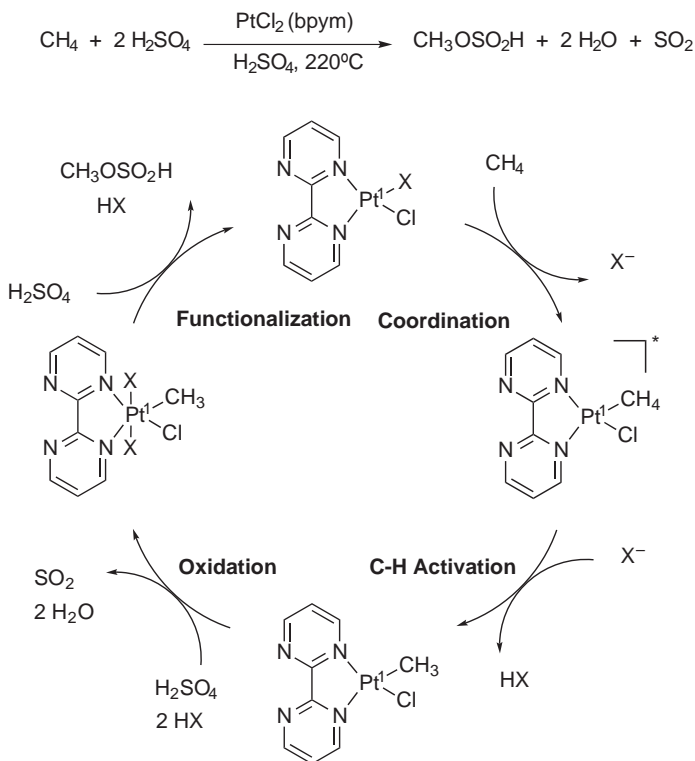


FIGURE 13.1 Proposed mechanism of the Catalytica system at 220°C in concentrated sulfuric acid. At 150°C, in D₂SO₄, there is incorporation of multiple D in the CH₄ but no conversion to oxygenated products has been observed. This indicates that reversible methane coordination and C–H cleavage occurs at a temperature lower than that required for oxidation.

13.1.2 Dimerization of Methane

The dimerization of methane to ethane and ethylene has been studied extensively. In the Benson process, methane is burned in chlorine in a highly exothermic reaction at an adiabatic flame temperature of 700–1700°C. As might be expected, huge amounts of hydrogen chloride are obtained, which must be reconverted to chlorine or used in some other way. This seriously inhibits commercialization of the process.

Catalytic oxidative coupling of methane has also been explored. Thus it has been shown that lithium-doped magnesium oxide in the presence of oxygen will extract hydrogen from methane to form methyl radicals, which in turn combine to produce ethane and ethylene at 720°C. Conversion is about 38% with a selectivity of about 50%. ARCO has been able to obtain conversions up to 15% with selectivities of 78% to C₂–C₇ compounds, mostly ethane and ethylene. One catalyst described is manganese acetate with sodium promoters. In other work nitrous oxide was used in place of oxygen.

In 1993 work at the University of Minnesota suggested the feasibility of oxidative coupling of methane to give ethylene at 830°C in the presence of oxygen and samarium oxide, Sm_2O_3 . Yields of 60% were claimed as opposed to previously achieved values of 25%. The key appears to be the shifting of equilibrium by the rapid removal of oxygen, methane, and ethylene. More recent work from Amoco (now BP) improves the oxidative coupling process by integrating the exothermic methane coupling reaction with an endothermic cracking of saturated hydrocarbons in a dual-flow reactor. The heat produced in the methane coupling reactor is transferred through the walls of the reactor tubes to the second cracking zone.

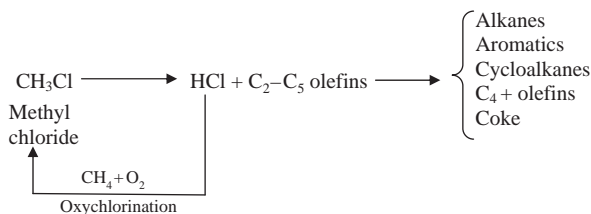
The direct conversion of methane to acetic acid with oxygen, rhodium chloride, and water at 100°C has been accomplished at Pennsylvania State University, although reaction rates are very low.

More recently, in 2010, Saluria Technologies described a nanowire-based catalyst that effected the transformation of methane to ethylene by way of oxidative coupling. Dow and BASF are said to be among a dozen or so companies with similar objectives.

13.1.3 Aromatization of Methane

The conversion of methane to aromatics has been studied by BP. The aromatization is accomplished in the presence of an oxidant, nitrous oxide, with an acid catalyst, a gallium-doped H-form zeolite. Methane conversion of 39% per pass has been reported with selectivities to aromatics of 19%. Although such results are promising, the economics are doubtful because 1 mole of nitrous oxide is consumed for every two C–H bonds that are broken. Also, additional oxidant is consumed in the undesirable formation of carbon oxides. The conversion of the stoichiometrically used oxidant to a catalyst, as we saw in the vinyl chloride process (Section 5.4) would provide a solution as would a cheaper process for producing nitrous oxide or an effective but cheaper catalyst.

As mentioned above, methane can be halogenated under mild conditions. In a proposed process for converting methane to gasoline, chloromethane is dehydrohalogenated under conditions such that coupling takes place simultaneously to give $\text{C}_2\text{--C}_5$ olefins. These, under the conditions of the reaction, recombine to provide gasoline-range paraffins and aromatics. Some olefins are also produced. In the process hydrogen chloride is evolved and is reused for oxychlorination of the methane:



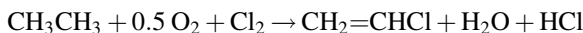
A report from the University of Minnesota indicates that platinum or rhodium catalysts effect the conversion of methane to synthesis gas (Section 12.4) at ambient temperatures. Selectivity and conversions are reported to be high.

13.2 FUNCTIONALIZATION OF C₂–C₄ ALKANES

The commercialized reactions in which alkanes have been oxidized were listed at the beginning of this chapter. Several interesting processes, one of which has reached pilot plant stage, have been described in the literature.

13.2.1 Oxidation of C₂–C₄ Alkanes

The oxychlorination of ethane to vinyl chloride may be carried out with a metallic silver/manganese catalyst in combination with other compounds such as lanthanum salts, either in the particulate form or impregnated on a zeolite, to provide vinyl chloride at 400°C and atmospheric pressure.



Contact time is 1–2 seconds. Complete conversions can be obtained with selectivity to vinyl chloride as high as 50%. This process, patented by ICI, showed promise, and commercialization was predicted by about 2005, but it has not happened (Section 5.4). It is not clear how far this process overlaps with the EVC process described below. An earlier process devised by Lummus using conventional oxychlorination catalysts yielded selectivities of 37% at 28% conversion. Geon and OxyChem worked on the same reaction but with less success.

Monsanto studied the oxychlorination of ethane to vinyl chloride in a vapor phase fluidized bed reactor with a catalyst comprising alumina-supported copper halide and potassium phosphate at 550°C. Ethyl chloride is a by-product, which can subsequently be oxidatively dehydrogenated to vinyl chloride. Ethylene dichloride by-product can be cracked by conventional means to vinyl chloride. Conversions on the order of 85–90% based on hydrogen chloride can be achieved with selectivities as high as 87% based on ethylene.

EVC (now INEOS Vinyls) appears to have made the breakthrough in the generation of VCM directly from ethane.⁸ Ethane is catalytically oxychlorinated to vinyl chloride in an integrated multistep process. Because a significant amount of chlorinated hydrocarbons, both saturated and unsaturated, are formed in the primary oxychlorination stage, it is critical to the economics of the process to recycle the by-products to reduce wasted feedstock. The unsaturated chlorinated by-products are converted to saturated products by a separate hydrogenation stage and then dehydrochlorinated to vinyl chloride. By recycling the by-products, a very high overall vinyl chloride yield is achieved. The EVC process operates at low temperatures relative to earlier attempts at ethane oxychlorination. This is crucial as high temperatures and a chlorine-containing environment are extremely corrosive, and the metallurgy required to contain such a system is exotic and expensive. The EVC process has been tested in a pilot plant at Wilhelmshaven, Germany. EVC also claims a 20–30% reduction in production costs across the PVC chain while the process decouples VCM/PVC production from the ethylene cracker.⁹ This process seems to have much

in common with the ICI process above. Dow has also worked on a process and produced a mechanism for the reaction.¹⁰

In the mid-1980s, Union Carbide developed the Ethoxene (Section 13.2.2) process to produce acetic acid via the catalytic gas phase oxidation of ethane. The problem was the simultaneous production of substantial quantities of ethylene as well as acetic acid, and development of it was abandoned. In 2000, SABIC announced its intention to build a pilot plant based on catalytic ethane oxidation using its own proprietary process, which makes acetic acid in selectivities of up to 60% with little or no ethylene coproduct.¹¹ This might be an economic source of acetic acid, given the low-cost ethane available to SABIC. A 30,000 metric ton/year pilot plant came on stream in 2005 in Yanbu.

The ammoxidation of propane to acrylonitrile was been studied for many years by BP and was targeted for commercialization in the late 1990s, but has made no progress, perhaps because of BP's sale of its chemical interests. The reaction is postulated to proceed by way of a propylene intermediate. One proposed catalyst, in an early patent issued to another developer, Monsanto, comprises a mixture of antimony and uranium oxides with a halogen promoter such as methyl bromide.¹² Antimony was a first generation and uranium a second generation catalyst for the ammoxidation of propylene (Section 6.5). Reaction takes place at 500°C to give 71% selectivity at 85% conversion for a yield per pass of 60%. Raw material savings are somewhat eroded by the higher capital costs of the process. Newer patents describe catalysts comprising a mixture of vanadium, antimony, phosphorus, and cobalt as well as bismuth, vanadium, molybdenum, chromium, and zinc. These provide lower yields per pass but may have other advantages. In addition to BP, two Japanese companies, Asahi Chemical and Mitsubishi Chemical, have been active in developing propane ammoxidation processes that can be run in two modes. One mode requires operation at modest per pass propane conversions to maintain high selectivities to acrylonitrile. This requires unreacted propane to be recycled and necessitates the use of oxygen instead of air, because the nitrogen in the air builds up in the recycle loop. The alternative mode is to run at high conversions per pass without recycling the unreacted propane. This route has higher propane consumption but permits the use of air as the oxidant. It remains to be seen which approach, if either, will eventually be commercialized.¹³

Catalytic oxidation of propane to acrylic acid is also under development.¹⁴ Promising patents have been awarded to Mitsubishi Chemical, Toagosei, BASF, and Sunoco. An effective MoVTenbO oxide catalyst for propane selective oxidation to acrylic acid had a metal atomic ratio Mo₁V_{0.31}Te_{0.23}Nb_{0.12}. The conversion of propane and the maximum yield of acrylic acid reached about 50% and 21%, respectively. No commercialization plans have been announced thus far. The yield to acrolein and acrylic acid combined is 85%. BASF has patented a propane-to-acrylic acid process said to give a combined yield to acrolein and acrylic acid of 85%.¹⁵

Catalytic oxidation of *n*-butane to maleic anhydride was discussed in Section 7.4.2. This process, commercialized more than 30 years ago, is still the only transition metal catalyzed alkane activation process to achieve widespread use. Spin-offs of this technology are processes to convert *n*-butane to 1,4-butanediol and tetrahydrofuran

(Section 7.1.6.5). These processes all proceed via hydrogenation of maleic anhydride or maleic acid. As far as the alkane activation component of the process is concerned, they are simply variations on the maleic anhydride technology.

In a reaction analogous to the oxidation of butane to acetic acid, propane or a propane/butane mixture can be oxidized at about 450°C and 20 bar to acetaldehyde and a large number of other oxygenated compounds. The reaction can be conducted either in the liquid or gaseous phase and has been used commercially in the United States. In a related development, ICI oxidized ethane in the presence of hydrogen chloride to acetaldehyde. A silver manganate catalyst, AgMnO_4 , is used at 360°C. Conversion was 14% and selectivity to acetaldehyde is 71%. Chlorinated by-products such as methyl and ethyl chloride can be recycled to inhibit their additional production.

13.2.2 Dehydrogenation of C_2 – C_4 Alkanes

Dehydrogenation of ethane, propane, or butane to the corresponding olefins is an alternative to steam cracking that requires higher temperatures and greater capital investment. Nonetheless, as the worldwide demand for polypropylene continues to grow, there is concern that conventional sources of propylene will be inadequate. Propane dehydrogenation (Section 6.1) is a route to propylene that is now well developed.

n-Butane is seldom if ever dehydrogenated because of the large energy input required. The dehydrogenation of butenes to butadiene is carried out commercially in the United States (Chapter 7). A further C_4 dehydrogenation reaction currently in use involves conversion of isobutane to isobutene, the latter being required for the declining market for MTBE (Section 7.2.1). The reaction takes place readily, unlike most dehydrogenations, because the tertiary hydrogen is an excellent leaving group. Isobutane is also used as feedstock for propylene oxide (Section 6.8). The isobutane is oxidized with air to *tert*-butyl hydroperoxide, which is used as the source of oxygen in the catalytic epoxidation of propylene to propylene oxide. *tert*-Butanol is a by-product of this reaction. It can be dehydrated to isobutene for reaction with methanol over acidic ion exchange resins to yield MTBE. Alternatively, the *tert*-butanol can be directly converted to MTBE. For obvious reasons, this approach to propylene oxide production is not expected to grow. Dehydrogenation of isopentane has been used to make isoprene.

Petroleum wax fractions from lubricating oil dewaxing can be dehydrogenated to α -olefins. Hydroformylation (Section 6.9) then gives detergent range alcohols. For instance, Sasol in Augusta, Italy, uses UOP's Pacol process to dehydrogenate paraffins and separates the product olefins from the starting paraffins by UOP's Olex process. These processes could possibly be improved if oxidative dehydrogenation were possible. Thus far successful processes have not evolved, because the products oxidize more readily than the starting material. Meanwhile, wax cracking has been used in the past in Italy and by Chevron to obtain an *n*-alkane/olefin (not necessarily α) mixture used to alkylate benzene to give alkylbenzenes for detergent use.

The dehydrogenation of ethane to ethylene is more difficult than that of the higher hydrocarbons. Many companies have worked in this field. Union Carbide, as indicated earlier (Section 13.2) devised an oxidative dehydrogenation in the vapor phase to produce a mixture of ethylene and acetic acid. The ratio of the two products can be varied from 1:1 to 5:1. The catalyst comprises molybdenum and vanadium doped with niobium, antimony, and one other metal, which can be calcium, magnesium, or bismuth. The reaction takes place at 330–435°C with conversions of approximately 30% and selectivities as high as 90%. Although this might provide a convenient route to acetic acid without requiring the investment for dedicated plants, the imbalance between global ethylene and acetic acid demand (114 versus about 7.5 million metric tons in 2009) means that it could never be the sole source of ethylene. If it were, a large surplus of acetic acid would be produced.

13.2.3 Aromatization of C₂–C₄ Alkanes

Since ease of aromatization increases with molecular weight, ethane aromatizes more readily than methane, and propane and butane aromatize more readily than ethane. The dehydrocyclization of alkanes, primarily propane and butane or liquefied petroleum gas (LPG) to aromatics, provides the basis for BP's and UOP's Cyclar process, for which a demonstration plant was operated in the early 1990s. In 1999 a plant came on stream in Saudi Arabia. It processes 1.3 million metric tons/year of LPG to produce 350,000 metric tons/year of benzene, 300,000 metric tons/year of *para*-xylene, and 80,000 metric tons/year of *ortho*-xylene.¹⁶

The Cyclar process uses a propane–butane mixture (LPG) in a reaction maintained at 535°C and 6 bar with a contact time of 14 seconds. Twenty-nine percent conversion with 95% selectivity to aromatics results. The process is useful as a source of benzene in Saudi Arabia where pyrolysis gasoline (Section 4.5.1) is not available and where very little catalytic reforming is done (Section 4.8). The BTX distribution with propane and butane as feeds is shown in Table 13.1.

The aromatization of ethane takes place with a gallium or platinum-doped ZSM-5 zeolite catalyst. The shape-selective property of the catalyst (cf. Section 10.1, toluene disproportionation) promotes the selective formation of cyclohexane and methylcyclohexane. Dehydrogenation provides benzene and toluene. The inlet temperature is about 700°C. Because the reaction is endothermic, a high input of heat per kilogram of ethane converted is required. The reaction is carried out at 2 bar and the ethane

TABLE 13.1 Aromatics Yield (%) from Aromatization of Propane and Butane

	Propane	Butane
Benzene	32.0	27.9
Toluene	41.1	42.9
Xylenes	18.9	21.8
C ₉ and C ₁₀ aromatics	8.1	7.4

conversion per pass is about 33%. Of this, 30 mol % is methane and 60% is benzene and toluene. Less than 2% higher hydrocarbons result.

13.3 CARBON BLACK

Many petrochemical processes are seriously hindered by the formation of carbon, which poisons catalysts and blocks furnace tubes. Thermodynamically, alkanes incline toward carbon and hydrogen as the most stable products. The production of carbon from alkanes, including methane, is thus relatively easy.

Carbon black is an amorphous graphite or soot consisting of highly aromatic carbon structures of colloidal size. It is made by partial combustion or combustion plus thermal cracking of hydrocarbons at 1300–1400°C. The feedstock may be an alkane or olefin or almost any hydrocarbon. Methane was once used widely but is no longer economic. Gas oil and residual oils are now popular especially from sources high in aromatics.

Many grades of carbon black are produced, varying primarily in particle size (between 10 and 500 nm) and surface area but also in other properties important in rubber compounding. This mature carbon-black technology has been slightly perturbed by the appearance of nanoparticles, a term generally used to indicate particles with dimensions less than 100 nm, so that traditional carbon blacks overlap with the nanoparticle region (Section 18.11). The smallest nanoparticles, only a few nanometers in diameter, contain only a few thousand atoms. These particles are called quantum dots and can possess properties that are entirely different from the bulk materials.

Nanostructured silica–carbon powders of the kind that could be used in tires are made in a so-called turbulent diffusion flame reactor based on a conventional

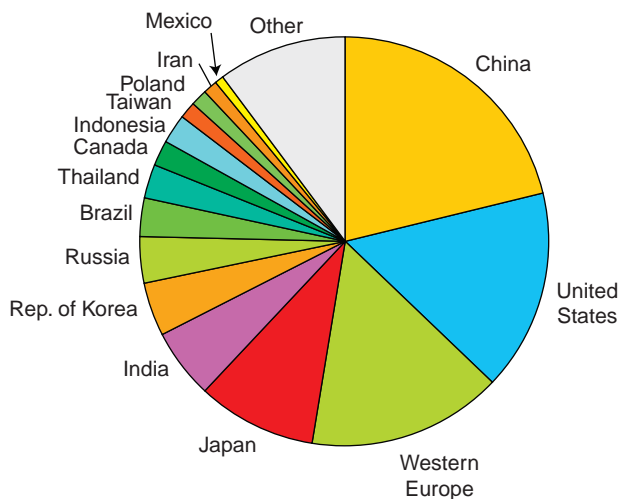


FIGURE 13.2 World consumption of carbon black by country (2007).

hydrogen–air burner. Hexamethyldisiloxane is fed into the flame and the products collected. Pure silica and composite silica–carbon nanoparticles result from the oxidation of hexamethyldisiloxane $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$.

The combination of carbon black and silica is more effective in reinforcing rubber than carbon black alone, providing the capability for manufacture of “green tires.” The silica surface is covered with silanol groups so that the addition of an organosilane coupling agent forms a silica network in the rubber. This filler-to-filler network enhances the tire reinforcement, and decreases the rolling resistance by up to 24%, while wet traction and tread wear are similar to conventional tires. Fuel consumption is significantly decreased as is air and environmental pollution. The problem, of course, is the price. The siloxane starting materials are not cheap and the products market at \$5.5–11 per kilogram, compared with typical carbon black prices of \$0.90 per kilogram.

The global market for carbon black in 2009/2010 was 9 million metric tons.¹⁷ In 2007, 72% went into tires to provide abrasion resistance and mechanical strength to the rubber; 20% went into other elastomers and the remaining 8% into printing inks, paints, and plastics. The U.S. carbon black market has declined from about 1.6 million metric tons in the early 1970s to about 1.1 million metric tons in the early 2000s. This is partly because automobile tires now last longer. Mainly, however, with the global automobile industry moving east to China, India, and Eastern Europe, the tire industry has followed, and with it the carbon black producers. More automobiles are imported into the United States. The availability of natural rubber in Southeast Asia is also a factor in the tire industry’s investment pattern. Hence other countries are significant consumers, as indicated in Figure 13.2.

ENDNOTES

1. Japanese patents 189,249–250 (27 November 1981) to I. Masakazu describe the oxidation of methane with nitrous oxide to methanol and formaldehyde.
2. Mitsui Chemical’s catalytic oxidation of ammonia to nitrous oxide is described in U.S. Patent 5,849,257 (15 December 1998).
3. Catalytica’s mercury-based catalyst is described in U.S. Patent 5,305,855 (26 April 1994) and the platinum-based catalyst is described in World Patent 98/50333 (12 November 1998).
4. M. Ahlquist, R. A. Perianab, and W. A. Goddard III, *Chem. Commun.*, 2373–2375, 2009.
5. E. Davies, *Chemistry World*, February 2009, pp. 51–54.
6. <http://www.nano.org.uk/news/938/>.
7. *Chem. Week*, 5 July 2010, p.15; *Chem. Eng. News*, 17 January 2011, p. 20.
8. EVC’S ethane to VCM process is described in a series of patents: EP 0 667 844B1 (4 February 1998), WO 95/07252 (16 March 1995), WO 95/07251 (16 March 1995), WO 95/07250 (16 March 1995), WO 95/07249 (16 March 1995).
9. <http://www.icis.com/v2/chemicals/9076569/vinyl-chloride/process.html>; ICIC Chemical Business, 17–23 January 2011.

10. E. E. Stangland, D. A. Hickman, M. E. Jones, M. M. Olken, and S. G. Podkolzin, <http://www.nacatsoc.org/20nam/abstracts/O-S3-10.pdf>; M. M. Olken, D. Hickman, and M. Jones, <http://www.nacatsoc.org/20nam/abstracts/P-S2-01A.pdf>.
11. <http://www.icis.com/Articles/2000/11/14/126388/sabic-develops-new-ethane-oxidation-acetic-acid-process.html>.
12. An early Monsanto patent is West German Patent 2056,326. Mitsubishi Chemical patents on propane ammoxidation include U.S. Patent 5,750,760 (12 May 1998) and WO 98/22421 (28 May 1998). Asahi Kasei patents on this subject include U.S. Patent 5,780,664 (14 July 1998) and U.S. Patent 5,663,113 (2 September 1997).
13. M. Olga Guerrero-Pérez, J. L. G. Fierro, M. A. Vicente, and M. A. Bañares, *Chemistry of Materials*, **19** (26), 6621–6628, 2007; *Journal of Physical Chemistry C*, **111** (3), 1315–1322, 2007.
14. Wei Zheng, Zhenxing Yu, Ping Zhang, Yuhang Zhang, Hongying Fu, Xiaoli Zhang, Qiquan Sun and Xinguo Hu, *J. Natural Gas Chem.*, **17** (2), 191–194, 2008.
15. U.S. Patent 6,541,664 (1 April 2003).
16. <http://www.uop.com/objects/46%20Cyclar.pdf>.
17. <http://www.sriconsulting.com/CEH/Public/Reports/731.3000/>.

CHAPTER 14

Chemicals from Coal

We have described the derivation of chemicals from petroleum and natural gas. But between 5% and 10% of organic chemicals come from other sources – coal, fats and oils, and carbohydrates. Historically these sources are important, because it was from them that the modern chemical industry evolved. Their present applications are also significant, particularly for specialty chemicals. Furthermore, because fats, oils, and carbohydrates are renewable resources, they represent an insurance policy for the future.

Coal, although a nonrenewable source of chemicals and energy, occurs on earth in much larger quantities than petroleum. Proven reserves will last for 118 years at the present (2010) rate of consumption, and are twice those of petroleum. The oil figure excludes shale oil except for 26.5 billion barrels credited to Canada for oil sands “under active development.” In 2000, the figure was 210 years, indicating the increasing use. Although seen as polluting and difficult to handle, it still accounts for 29% of world energy consumption. Different regions consume different amounts. Coal only accounts for 1.4% of Middle East energy consumption, awash as they are with oil. It accounts for 16% of European Union energy consumption, 24% of U.S. consumption, and a staggering 71% of Chinese consumption. In Western Europe, coal seams are narrow and deeply buried, but in other parts of the world open-cast mining is attractive. The contribution of coal to world energy is growing and, in 2009, reached its highest share since 1982. China has moved from being a coal exporter to being a major importer; her total imports of coal in 2010 were a record 126 million metric tons, treble the 2008 level. We shall discuss coal first, before we turn to the renewable sources.

Coal, however polluting and dangerous to extract, is no longer a poor relation. The fact that it is a solid and difficult to handle is a drawback in developed countries; skilled engineers find it more economic to pump gases and liquids. Developing countries, with quantities of cheap labor and accessible coal deposits, find it an attractive low technology option, providing both employment and an energy supply.

Coal powered the Industrial Revolution in Britain, where it all happened. “King Coal” provided work for one million men, perhaps one in ten of the UK male working population. At its peak, before the First World War, Britain produced 287 million tons of coal in a year.¹ Coal was traditionally important to the chemical industry in the nineteenth and early twentieth centuries. It provided carbide and hence acetylene (Section 14.7), synthesis gas (Section 14.5) hence ammonia and methanol, petroleum-like fuels, and all the aromatic chemicals contained in coke oven distillate. This distillate still provides some chemicals, although the quantities (very approximately 1.5%) pale by comparison with those from petrochemicals. It still provides about 5% of world benzene (see Fig. 9.1) and is the major source of polynuclear aromatics.

Coal (town) gas, producer gas, water gas, and synthesis gas are often confused. An explanation is offered in Table 14.1. The conversion of coal to synthesis gas (Section 14.5) was developed in the nineteenth century as a source of fuel. It was mixed with oil gas to increase its calorie content. That coal-based synthesis gas can still provide the basis for chemicals was demonstrated most recently by the Eastman acetic anhydride process (Section 12.5.2.3). Coal-based synthesis gas is also the basis for the Fischer–Tropsch reaction as initially practiced (Section 14.2). It could be used for substitute natural gas (Section 14.5) but this has not been commercialized. The hydrogenation of coal is another approach to converting coal to liquid fuels and conceivably to raw materials for chemicals.

Although there is no interest in the early 2000s in substitute natural gas or coal hydrogenation, the Fischer–Tropsch reaction has come into prominence as a means of converting “stranded” gas to a liquid form for easy transportation (Section 12.7).

TABLE 14.1 Coal-Based Gas Mixtures

Name	Origin and Composition
Coal or town gas	A coproduct of coke oven operation, mainly hydrogen (50%), methane (35%), and carbon monoxide (10%).
Producer gas	A low BTU gas with a high nitrogen content, made by passage of air and steam over coke. It is now obsolete.
Water gas (blue gas)	The gas obtained from the passage of steam over coke at about 1000°C. Its composition is typically 40% CO, 50% H ₂ , 5% CO ₂ , and 5% N ₂ and CH ₄ . A gas with higher H ₂ :CO ratio is obtained by steam reforming of methane and higher alkanes.
Synthesis gas	For the manufacture of chemicals, synthesis gas is required with various CO:H ₂ :N ₂ ratios. This can be based on coal via water gas or from natural gas or petroleum hydrocarbons. See Section 12.4 and Figure 12.2.
Oil gas	Obtained in the United States by thermal cracking of petroleum distillates. It contained 20–25% ethylene, 13–16% propylene, and some higher olefins and light paraffins. Oil gas was not available in Western Europe.
Substitute natural gas (SNG)	Methane made by gasification of coal or petroleum fractions. See Section 12.4.

After World War II, enthusiasm for coal-based chemicals waned as the cost of petrochemicals dropped. Interest increased in the 1970s at the time of the oil shocks but waned again in the 1980s because the price of petroleum dropped and there were huge discoveries of natural gas around the world especially in the former Soviet Union, the Gulf area especially Qatar, and Indonesia. Interest has since revived in China.

14.1 CHEMICALS FROM COKE OVEN DISTILLATE

When coal is heated in the absence of air to a temperature of about 1000°C, coke forms together with a number of liquid and gaseous decomposition products. It is this distillate, also called coal tar, that provided the aromatics and many other chemicals for the early chemical industry. One metric ton of coal yields about 37 kg of tar. Some of the chemicals are shown in Figure 14.1.

The coke is almost pure carbon and is used in steel manufacture which, as it becomes more efficient and processes change, requires less coke. Nonetheless, some coke will always be needed, and therefore the chemical industry will always have available the chemicals that volatilize from the coke ovens. Current global annual production of coal tar is on the order of 20 million metric tons.

A typical coking operation produces 80% coke by weight, 12% coke oven gas, 3% tar, and 1% light oil consisting of crude benzene, toluene, and xylenes as well as over 200 other chemicals. The U.S. production of coal tar is the same order of magnitude as a medium tonnage chemical such as butadiene, but is still less than a third of what it was in the 1950s. The coal tar is distilled to give four fractions:

1. Light oils, boiling below 200°C. They are called light oils because they float on water. They are crudely fractionated, then agitated with concentrated sulfuric acid to remove olefins. The hydrocarbons are washed with dilute sodium hydroxide and redistilled to give benzene, toluene, xylenes, and “solvent naphtha,” a mixture of indene, coumarone, and their homologs. This is a powerful solvent especially for coatings containing coal tar and pitch, whose use has decreased markedly. Treated with a Friedel–Crafts catalyst such as aluminum chloride, it gives coumarone–indene thermoplastic resins, used for cheap tiles, varnishes, and adhesives.
2. The middle oils boil between 200°C and 250–270°C. The most abundant chemical is naphthalene and it occurs with phenols, cresols, and pyridines in the tar. It crystallizes when the middle distillate from the tar is allowed to cool and, even in this impure form, is suitable for phthalic anhydride manufacture (Section 11.1). Alternatively, it may be purified by sublimation, a somewhat unusual purification process, in which the material passes directly from the solid to the gaseous phase. Extraction of the remaining tar with aqueous sodium hydroxide takes the acidic phenols and cresols into the aqueous layer as phenates and cresylates. They are regenerated with carbon dioxide. Subsequent extraction of the remaining oil layer with acid gives nitrogen-containing bases, primarily pyridines.

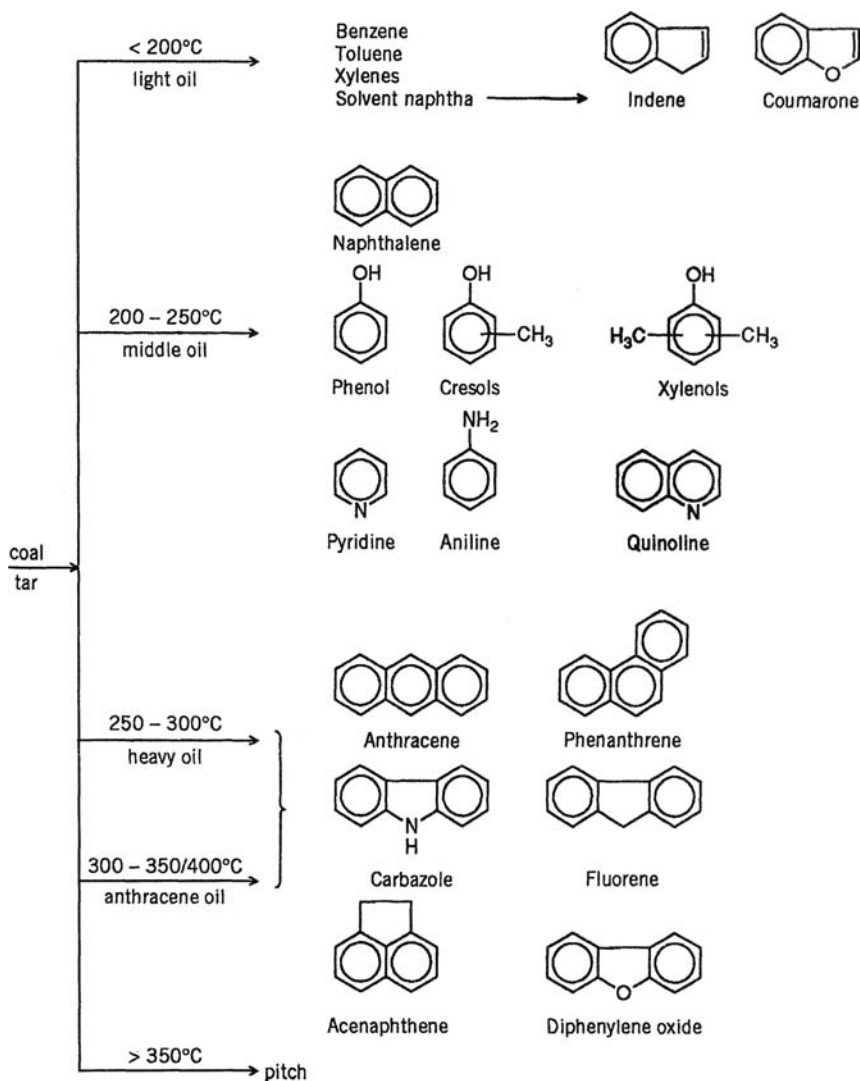


FIGURE 14.1 Coal tar distillation: major and some minor products.

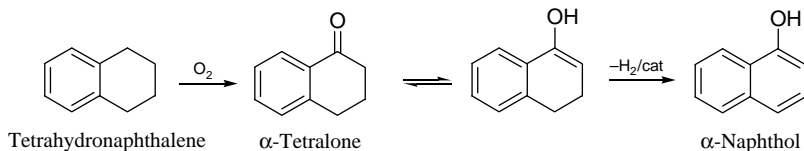
- Heavy oil comes off between 250°C and 300°C if anthracene oil is taken off as a separate fraction, but sometimes they are combined. It is used for wood preservatives generally under the name of creosote or (if the fractions are not separated) anthracene oil.
- Anthracene oil comes off between 250°C and 300/400°C or 350°C and 400°C if taken off as a separate fraction. It contains anthracene, phenanthrene, carbazole, and many other compounds in small quantities. It makes up about 1% of coal tar.

Some 60% of the tar remains as a residue called pitch. Its production is driven by the aluminum industry, which thermally polymerizes the pitch to make electrodes for the electrolysis of molten alumina/cryolite mixtures to give aluminum. The generation of each metric ton of aluminum consumes 0.45–0.6 metric ton of carbon, which is oxidized to carbon dioxide and monoxide. The use of carbon electrodes rather than an inert metal reduces the voltage required for the electrolysis. By saving electricity in this way the system is acting efficiently as a fuel cell. Other uses for coal tar include roofing sealants and enamel coatings for underground pipelines. The residual tar is used for road building and in paints, primarily to waterproof subsurface structures. These often comprise combinations of the tar with epoxy resins (Section 9.1.2.1). Creosote (heavy oil) is used to preserve telephone poles and railroad ties. It is one of the very few materials that impregnate wood.

Benzene from coke oven distillate accounted for 7.5% of total benzene production in Asia-Pacific in the early 2000s and 3–4% in Europe, but only 1–2% in the United States (see Fig. 9.1). The type and quantity of chemicals in coke oven distillate vary with the type of coal and method of coking. Typically, in the most volatile fraction of coke oven distillate, benzene comprises 70%, toluene 15%, and the xylenes 4%. The remainder consists of alicyclics and aliphatics plus some phenols and cresols.

More important in market terms is naphthalene, which is a raw material for phthalic anhydride in competition with *o*-xylene (Section 11.1). Until the early 1960s, coke oven distillate was the sole source of naphthalene, but it can now be obtained by catalytic reforming of heavier naphthas. Unfortunately, methylnaphthalenes form, and the methyl groups must be removed by hydrodealkylation if naphthalene itself is desired. This is true also for naphthalenes from petroleum sources. The same reaction is used to convert toluene to benzene (Section 10.1). Annual naphthalene production in the United States in the early 2000s was about 265 million pounds. About 10% of production was petroleum-based. The remainder was from naphthalene from coke oven distillate.

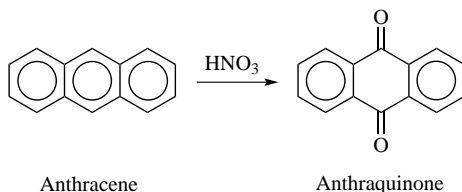
Naphthalene can be hydrogenated mildly to tetrahydronaphthalene (Tetralin) or vigorously to decahydronaphthalene (Decalin). Tetrahydronaphthalene has a number of applications. When there was great interest in the use of coal for chemicals, it was an effective hydrogen donor for coal liquefaction. It is currently used as a source of α -naphthol. Air oxidation gives α -tetralone and catalytic dehydrogenation gives α -naphthol, an important dye intermediate and also the starting material for the insecticide carbaryl (Section 12.5.2.6):



The anthracene and carbazole in anthracene oil are still useful to dyestuffs manufacturers. Anthracene is the starting point for anthraquinone dyes and carbazole

gives the Violet 23 shade of a popular chocolate bar wrapper, as well as the light-resistant Hydron blue dye used in several brands of blue jeans.

Before World War I, anthracene was concentrated sufficiently to enable it to be crystallized and the crude material oxidized to anthraquinone with nitric acid (as it still is) or dichromate.



During that war, the United States was cut off from anthraquinone and developed a synthetic method in which benzene reacted with phthalic anhydride in the presence of a Friedel–Crafts catalyst to give *o*-benzoylbenzoic acid (Section 9.8), which was dehydrated to anthraquinone. The method remained economically preferable to the coal tar extraction route until suspension crystallization techniques were developed in which the anthracene and carbazole were successively precipitated from copious quantities of high boiling aromatic solvents. Although cheaper than the synthetic route, there were various drawbacks. Unwanted products coprecipitated; the use of aromatic organic solvents was environmentally damaging, and the process consumed vast amounts of energy per kilogram of product.

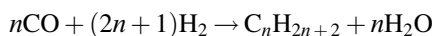
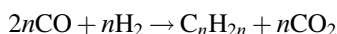
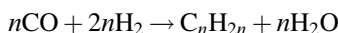
Rutgers, the only company currently processing coal tar in Germany, brought on stream a new plant for carrying out the separation in 2003 based on new technology.² In an industry as traditional as the coal tar industry, this was a major event. The method used relies on engineering innovations that permit melt crystallization at temperatures near 300°C. Liquid feed without solvent is gradually cooled by a series of vertical heat exchanger plates to encourage crystal growth on the surface of the plates. The liquid residue (sooty oil) is drained off. The plates are then heated very slowly enabling the crystals to “sweat away” further impurities. Melting of the remaining crystals produces a fairly pure phenanthrene–anthracene–carbazole mixture, which cannot be separated by crystallization because the compounds form solid solutions. Instead, they are separated by high temperature vacuum distillation, itself difficult because phenanthrene (at atmospheric pressure) boils within a degree of anthracene (bp = 339.9°C) although there is then an appreciable gap before carbazole (bp = 354.75°C).

The quantities of coal tar distillate available are limited by the demand for coke by the steel industry and could not be increased substantially to compensate for a shortage of petrochemical products. Changes in the coal chemicals field are described by McCoy.³

14.2 THE FISCHER–TROPSCH REACTION

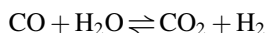
The Fischer–Tropsch reaction provides a route from coal to hydrocarbons.⁴ When synthesis gas (Section 12.4) at near atmospheric pressure is passed over an iron,

nickel, or cobalt catalyst at 150–300°C, a mixture of alkanes and olefins with a broad range of molecular weights is formed. The olefins are formed first and Sasol, which is one of the major operators of the process, isolates and sells them (Section 12.6.1). Alternatively, they may be reduced to alkanes. If hydrogen-rich synthesis gas is used, made from naphtha or methane instead of coal, alkanes may be the initial products (Section 12.4).



The hydrocarbons are predominantly C₅–C₁₁ straight chain, although methane, ethylene, and propylene are also produced together with some higher molecular weight Fischer–Tropsch waxes used for candles. There are also oxygenated compounds such as alcohols and acids. The result is a petroleum-like mixture that can be used as both a fuel and a chemical feedstock. Ruthenium⁵ has been proposed as a catalyst for higher molecular weight hydrocarbons. Both fixed and fluid bed processes are operated and the products are shown in Table 14.2.

The mechanism of the Fischer–Tropsch reaction is complex and has not yet been completely elucidated. It is generally agreed that the above processes are basic. The water gas shift reaction also takes place but requires an iron catalyst.



Its equilibrium can be directed either way depending on temperature, pressure, and reactant concentrations. Undesirable reactions include the formation of

TABLE 14.2 Fischer–Tropsch Products as Obtained at Sasol

Product	Fixed Bed at 220°C (wt %)	Fluidized Bed at 325°C (wt %)
CH ₄	2.0	10
C ₂ H ₄	0.1	4
C ₂ H ₆	1.8	4
C ₃ H ₆	2.7	12
C ₃ H ₈	1.7	2
C ₄ H ₈	3.1	9
C ₄ H ₁₀	1.9	2
C ₅ –C ₁₁ (gasoline)	18.0	40
C ₁₂ –C ₁₈ (diesel fuel)	14.0	7
C ₁₉ –C ₂₃	7.0	–
C ₂₄ –C ₃₅ (medium wax)	20.0	4
C ₃₅ + (hard wax)	25.0	–
Water-soluble nonacid chemicals	3.0	5
Water-soluble acids	0.2	1

methane; the disproportionation of carbon monoxide to carbon dioxide and carbon; and the oxidation of the metal catalyst. Formation of carbon fouls the catalyst. Addition of steam inhibits carbon formation and depresses slightly the yield of methane.

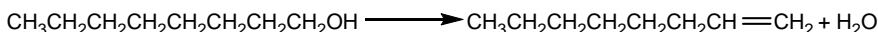
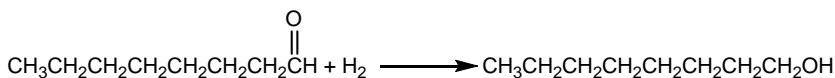
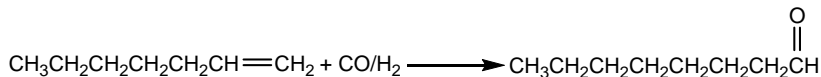
Since the hydrocarbons are straight chain, they have low octane numbers and must be isomerized for use as gasoline or in the alkylation reaction (Section 4.10). On the other hand, the straight chain structure is ideal for steam cracking and catalytic reforming to provide the olefins and aromatics needed for chemical synthesis.

The process was subject to intensive development between the world wars and was operated successfully on a large scale in Germany during World War II. Currently, Fischer–Tropsch processing is underway in South Africa in three plants. It was by this means that the old South Africa protected itself because its racial policies provoked a petroleum boycott. A change of government in the 1990s has obviated this need. Fuel production has continued because the increased cost of oil makes it economical in depreciated plants. The Fischer–Tropsch products are created by growth of carbon chains on an iron-based catalyst and there is no restriction on their size. Thus a range of alkanes of varying molecular weights, many of them useless for gasoline, are produced. Initially these by-products were burned as fuel but are now being “mined” for chemicals. The Fischer–Tropsch “Synthol” fuel stream contains a range of α -olefins of all carbon numbers (odd and even) from ethylene through decene-1, whereas ethylene oligomerization, the conventional route to α -olefins, gives only even carbon numbered compounds (Section 5.3.2). The first α -olefins to be produced were in the pentene to octene range.⁶ Availability generally decreases with increasing carbon number.

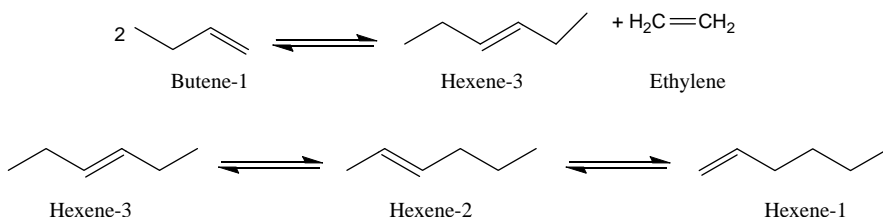
α -Olefins in the butene-1 to octene-1 range can be used as linear low density polyethylene comonomers. Sasol has taken advantage of its access to low cost hexene-1 and octene-1 and has become a major supplier of these α -olefins. Pentene-1 also has potential application as a comonomer, but its adoption has been slow. In the past, it was not available and, even now, there is only a single supplier.

Sasol commenced 1-hexene production in 1994 and has since expanded to its current capacity of 250,000 metric tons per year. Its 1-octene capacity is 96,000 metric tons per year. Sasol’s first commercial on-demand octene-1 plant was commissioned in Secunda, South Africa, in 1998. This extraction-based technology consists of a combination of acid extraction, and normal, extractive, and azeotropic distillation techniques that extract and purify octene-1 from a fuel stream. Rapid growth in comonomer demand led to the construction of a second octene-1 plant, which was commissioned in 2004.⁷

A limitation to Sasol’s approach of extracting α -olefins from their synthetic fuel streams is that, once all the 1-hexene and 1-octene is extracted, there is no further way to expand capacity. This has stimulated Sasol to develop alternative techniques, such as ethylene tetramerization, described in Section 5.3.3. Another approach Sasol is developing is based on extracting 1-heptene. While there is no market for 1-heptene, it can be hydroformylated to an intermediate for 1-octene. Sasol commissioned a 100,000 metric ton/year hydroformylation plant in 2008:

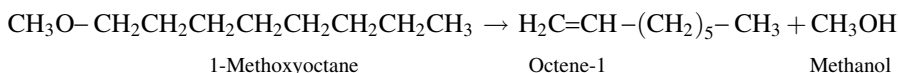
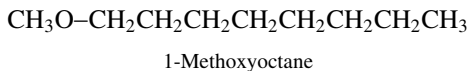
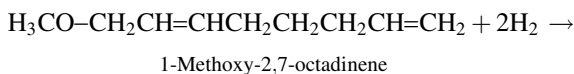
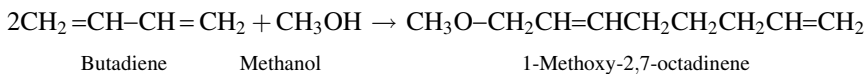


In competition with Sasol's processes are two non-coal-based routes to hexene and octene. Lummus has developed a metathesis route to 1-hexene, termed Comonomer Production Technology (CPT). It uses steam cracker C_4 s to replace what would otherwise require the more expensive polymer grade ethylene. It employs the so-called autometathesis of butene-1 to give hexene-3. The hexene-3 is finally isomerized to give 1-hexene. The idealized chemical reactions are



A difficulty with this approach is that both the metathesis and isomerization reactions are equilibrium controlled and can lead to side products and extensive recycle loops.⁸ Lummus's CPT process for hexene-1 production has been demonstrated in a joint venture with Sinopec at semicommercial scale.

Dow has been granted a patent⁹ describing the telomerization of butadiene with methanol in the presence of a palladium catalyst to yield 1-methoxy-2,7-octadiene. The 1-methoxy-2,7-octadiene is then hydrogenated to 1-methoxyoctane. Subsequent cracking of the 1-methoxyoctane gives octene-1 and methanol for recycle:



Dow started up a 50,000 metric ton per year octene-1 plant in 2007 in Tarragona, Spain, using this butadiene-based approach.¹⁰

The Fischer–Tropsch process does not produce the same balance of products as an oil refinery. When it was operated on a scale to meet South Africa's gasoline needs, insufficient diesel fuel resulted. Accordingly, additional processing was required, which led to an excess of gasoline. In the early 1990s, this had to be exported at uneconomical international prices. A similar problem afflicted Brazil's gasohol program when the replacement of gasoline by ethanol led to a diesel shortage.

In spite of its superficial virtues, the Fischer–Tropsch process with coal was generally felt to be costly and unreliable in operation. Coal is a solid; consequently, reactors were bulky, mechanically complex, and therefore expensive. Utility and maintenance costs were high, and coal had to be dug laboriously out of the ground. However, if one starts with gas rather than coal or coke (Section 14.7), the above objections disappear. Sasol is believed to use both coal and gas.

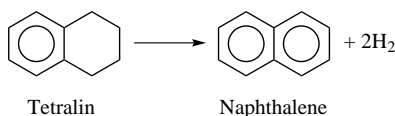
An alternative route to gasoline from synthesis gas is the Mobil MTG process described in Section 12.5.2.4. It uses molecular sieve catalysts whose pore size is sufficiently small to control the molecular weight within the C_5 – C_{10} range, so that the higher molecular weight alkanes produced in the Fischer–Tropsch synthesis are absent.

Workers at Utrecht University in the Netherlands have demonstrated ways of improving catalyst activity in the Fischer–Tropsch reaction by 50–60%.⁵ They control the morphology of a porous silica cast on which Co_3O_4 catalyst particles are deposited and obtain particles of uniform size that are evenly distributed. Other advances in catalysis are described by Milmo.¹¹

14.3 COAL HYDROGENATION

Coal has the approximate empirical formula CH . To convert it to an aliphatic hydrocarbon mixture requires addition of hydrogen. In the Fischer–Tropsch process, this is derived ultimately from water. It is, however, possible to hydrogenate coal directly. This process, called the Bergius process, was operated in Germany in World War II. Coal, lignite, or coal tar was hydrogenated over an iron catalyst at $450^\circ C$ and 700 bar, and 4 million metric tons of gasoline was synthesized in this way, largely for aviation fuel.

Less drastic conditions could be used for coal hydrogenation if a solvent could be found that would hydrogenate the coal in a liquid/solid phase process. In the hydrogen donor process, finely powered coal reacts for 1–2 hours with tetralin at about $200^\circ C$ and 65 bar. The tetralin acts as both a solvent and a hydrogen donor, giving up four hydrogen atoms to form naphthalene.

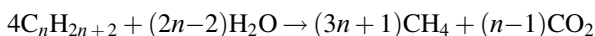


The hydrogen presumably reacts with free radicals generated by the coal decomposition to stabilize them and prevent further cracking, which would lead to gas formation. Free radical coupling, which leads to coke formation, is also prevented. The naphthalene produced is rehydrogenated to tetralin. The same technique can be used on heavy crude oils and on residues from crude oil distillation. The cheap petroleum of the late 1980s argued against commercialization of this process.

There are thus three routes from coal to petroleum-like fuels. The Fischer–Tropsch and Mobil processes are more attractive than the Bergius process. Whether or not coal ever becomes a raw material for petroleum-like fuels on a world scale depends on the severity of the petroleum shortage, the availability of the huge capital investment required, and the feasibility of various other possible sources of energy such as nuclear fission or nuclear fusion.

14.4 SUBSTITUTE NATURAL GAS

Methane made synthetically instead of by extraction from natural gas fields is known as substitute natural gas or SNG. The term “synthetic natural gas” is also used but is an oxymoron. In the 1960s and 1970s, rapid depletion of methane reserves seemed likely and, in the long term, coal seemed its logical source. So much natural gas has been discovered since then, however, that the process has not been widely adopted. SNG is nonetheless produced in Japan where natural gas is not available. It is made from petroleum fractions by a lower temperature variant of steam reforming.



In North Dakota, a Lurgi plant converts 1640 U.S. tons of lignite coal to 160 million cubic feet of substitute natural gas (SNG) by the Lurgi process. It has been operating since 1984. Anhydrous ammonia is used as a scrubbing liquid to remove sulfurous gases. Ammonium sulfate fertilizer results. There are other by-products including CO₂, which is said to be sequestered. Two coal-based plants are under construction in China.¹² Table 14.3 shows these and other coal-based plants in China.

The Catalytic Rich Gas (CRG) process (450°C, potassium promoted nickel catalyst) and the Gas Recycle Hydrogenator (750°C, no catalyst) are technologies that have been available for many years. The former, together with a variant called the “double methanation process,” requires a light naphtha feedstock, whereas the gas recycle hydrogenator can use heavier hydrocarbons.

14.5 SNG AND SYNTHESIS GAS TECHNOLOGY

Synthesis gas technology was discussed in Section 12.4. In principle, the conversion of coal or coke to synthesis gas is straightforward. The difficulty is one of solids handling. The various processes involve fixed beds, fluid beds, and entrained beds.

TABLE 14.3 Plants and Projects in China's Coal-to-Chemicals Industry

Company	Location	Technology ^a	Capacity (metric tons/year)	Startup	Project Status	Products
China Datang Corp.	Duolun Inner Mongolia	MTP	460,000	End 2010	Under construction	PP
Baotou Shenhua Coal Chemicals	Baotou Inner Mongolia	MTO	600,000	August 2010	Running stably	PP, PE
Shenhua Ningxia Coal Industry	Yinchuan Ningxia	MTP	500,000	October 2010	Test runs begun	PP
Tongliao Gold Coal	Tongliao Inner Mongolia	CTG	150,000	End 2009	Started up	Glycol
Qinghua Group	Yining Xinjiang	SNG	137,500	July 2011	Under construction	Synthetic natural gas
Xinwen Mining	Yining Xinjiang	SNG	200,000	October 2012	Under construction	Synthetic natural gas
Inner Mongolia Yitai Group	Ordos Inner Mongolia	CTL	160,000	March 2009	Running stably	Diesel, naphtha, liquefied petroleum gas

^aMTP = methanol to propylene (Section 12.5.2.5); MTO = methanol to olefins (Section 12.5.2.5); CTG = coal to glycol; SNG = substitute natural gas; CTL = coal to liquids.

Source: ICIS Chemical Business, 5 November 2010.

TABLE 14.4 Coal Gasification Processes

Process	Main Characteristics
Texaco	Pressurized entrained-bed process involving the use of a watery slurry of powdered coal. Less suitable for lignite. Product gas low in CH ₄ and tar-free. Low H ₂ /CO ratio (~ 0.7).
Lurgi	Pressurized moving-bed process suitable for noncaking granular coal. Relatively high steam consumption. Product gas is rich in methane, residual steam, and CO ₂ and contains tar; H ₂ /CO ratio ~ 1.7 .
Koppers–Totzek	Atmospheric entrained-bed process in which powdered coal is used as feed. Suitable for a wide range of coals. Relatively high oxygen consumption. Product gas low in methane, CO ₂ , and residual steam and free from tar; H ₂ /CO ratio ~ 0.5 .
Winkler	Atmospheric stationary fluid-bed process suitable for reactive coals (lignite). Moderate O ₂ and steam consumption. Moderately pure product gas. Moderate coal conversion. Operates at 800–1100°C.
High temperature Winkler (Rheinbraun)	Pressurized stationary fluid-bed process suitable for reactive coals (lignite). Higher gasification rates and more complete coal conversion than by Winkler process.
British Gas–Lurgi slagging gasifier	Pressurized moving-bed process primarily for noncaking granular coal. Less steam consumption, smaller reaction volumes and purer product gas than via Lurgi process.
Shell	Pressurized entrained-bed process in which a dry coal powder is used as feed. Suitable for wide range of coals including lignite. High thermal efficiency. Product gas of high purity, comparable to that obtained by Koppers–Totzek.

The main processes are summarized in Table 14.4. We shall comment only on the Lurgi process, the slagging gasifier and the Texaco processes.

The supply of steam and oxygen in a molar ratio between 2:1 and 6:1 to a moving bed of coal (replenished at the top with ash that was withdrawn at the bottom to provide effectively a fixed bed technology) leads to a mixture of hydrogen, carbon monoxide, carbon dioxide, and a little methane plus a mass of clinker (fused ash). The gases can be reformed, but the clinker is difficult to handle in a continuous plant. In the Lurgi process, developed in Germany in the 1930s, a high ratio of steam to oxygen was used that kept the temperature down and produced a gas high in methane and low in carbon monoxide plus a fine ash that could be handled in an appropriate grate. The excess steam is expensive and leads to large amounts of dilute but corrosive effluent. It also leads to increased plant size for a given capacity and a low thermal efficiency.

A British Gas process – the Westfield Slagging Gasifier – involved a low steam: oxygen ratio that gave a high proportion of carbon monoxide in the gas plus a slag that, at the high temperatures achieved, could be drawn off as a liquid.

The Texaco process, used by Eastman (Section 12.5.2.3), is a variant of the Koppers–Totzek process and involves an entrained bed. A stream of water carrying

pulverized coal meets a stream of oxygen creating a flame at 1400–1600°C, from which an SNG high in carbon monoxide and hydrogen and very low in methane and condensable hydrocarbons can be extracted. This is thermally inefficient because of the high temperature but the product is more suitable for chemicals than the moving bed processes. It cannot be used as SNG without further reforming.

14.6 UNDERGROUND COAL GASIFICATION

A very old method of coal gasification that is attracting renewed interest is underground coal gasification (UCG). Injection wells are drilled into a coal seam, and oxidants – air, oxygen, or steam – are pumped in and the coal ignited. Separate production wells bring the product gases to the surface. The high pressure combustion generates temperatures of 700–900°C but it may go up to 1500°C. The effluent gases are made up of carbon monoxide and dioxide, hydrogen, and small quantities of methane and hydrogen sulfide. As the coal face burns and the coal seam is depleted, the balance of oxidants is controlled by the operator.

The synthesis gas produced has a higher carbon-to-hydrogen ratio than oil- or gas-based synthesis gas. It is typically used to power combined cycle gas turbine plants (CCGT). CCGT power plants using UCG product gas instead of natural gas are said to achieve higher outputs than power stations based on pulverized coal. The product gases can also be used for synthesis of liquid fuels and for manufacture of ammonia and fertilizers. Furthermore, the UCG process results in a large decrease in greenhouse gas emissions. The process produces little solid waste, and acid gases can easily be removed. Combustion of the coal may lead to subsidence in a less controllable manner than traditional coal mining but is much less hazardous. There is a danger that trace organic contaminants (benzene, phenol) may be forced into groundwater.

UCG enables exploitation of coal seams that are too deeply buried or too thin. It has been estimated that it could increase U.S. recoverable coal reserves by 300% and world reserves by 600 billion metric tons.

UCG is a mature technology and has never really taken off. Much of the renewed interest is coming from China, but in 2009 Thornton New Energy was awarded the first UK UCG license to develop deep, previously unmineable coal reserves under the Firth of Forth, Scotland.¹³

14.7 CALCIUM CARBIDE

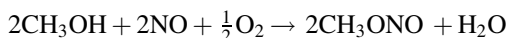
The production of acetylene by way of calcium carbide and its uses were discussed in Section 12.3. The process uses energy extravagantly and, at 2001 U.S. prices, the cost of electricity per kilogram of acetylene was greater than the total cost of a kilogram of ethylene. The use of carbide might have become attractive had cheap night-time electricity become available as a result of nuclear plants operating steadily around the clock. No new plants have been built since the Three Mile Island accident, however, so even if this is a possibility, it is in the distant future.

On the other hand, the Chinese seem to think acetylene is a worthwhile basis for a chemical industry and have built many carbide plants. Given present prices, carbide is easily the most economic route to acetylene.¹⁴

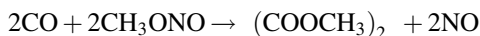
14.7.1 The Chinese Chemicals to Coal Program

The Chinese lack of oil and gas has prompted them to move “back to the future” and to revive many synthesis gas and acetylene-based routes to organic chemicals.¹² With the rise of oil and gas prices, the cheapness of coal makes the economics of coal-based processes more attractive. Vinyl chloride from acetylene is already a reality. Acrylonitrile, acrylic acid, butane-1,4-diol/tetrahydrofuran, chloroprene, and isoprene are thought to be the most economic forthcoming opportunities for acetylene use. The technology of these products is mature and the Chinese have experience in dealing with coal and acetylene.

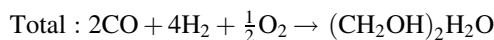
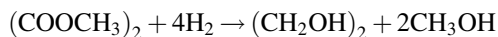
Table 14.3 shows current coal-based plants in operation or under construction. The technology of these has largely been discussed. The two relatively novel projects are still some way from commercialization. Coal-to-dimethyl ether as a one-step process from synthesis gas is of limited interest because of overcapacity for the product. Coal-to-glycol is more interesting and innovative.¹⁵ The process starts with syngas plus nitric oxide, oxygen, and methanol. The methanol reacts in the gas phase with the nitric oxide and oxygen to give methyl nitrite. A further reaction with carbon monoxide from the synthesis gas gives dimethyl oxalate. Hydrogenolysis with hydrogen, again from syngas, gives ethylene glycol and regenerates the methanol. Thus the methanol and nitric oxide fulfill a catalytic role.



Methyl nitrite



Dimethyl oxalate



Ethylene glycol

Tongliao Gold Coal started up a 150,000 metric ton/year plant at the end of 2009, but there are issues with catalyst technology.

A shift from conventional ethylene glycol (MEG) to coal-based MEG, pioneered by China, could shake up the world MEG market. MEG is used principally in the manufacture of polyester fiber. The global market in 2010 was 18 million metric tons of which China consumed 43% but produced only 12%.¹⁶ If the Chinese were to become a net exporter rather than an importer, there would be feedback into the ethylene and ethylene oxide markets in Western Europe and the United States. The economic impact of Chinese growth has been analyzed by KPMG.¹⁷

Meanwhile, major barriers to an extensive coal-based chemical industry in other parts of the world would be its price, which would need to be low to allow for the high capital costs of coal-processing equipment, and the amount of coal needed.¹⁸ Bayer estimated at the end of the 1970s that to produce all the organic chemicals then made from petroleum would require an extra 250 million metric tons of coal per year in Western Europe. Total current production of hard coal, lignite, and brown coal, not all suitable for chemicals, is only 400 million metric tons.

14.8 COAL AND THE ENVIRONMENT

Coal poses social and political as well as technical problems. The cheapest way to mine coal is by open pit or strip mining, which ruins large areas of countryside. On the other hand, traditional underground mining is a dangerous and expensive business that demeans the human spirit. The British coal industry is a historic one, and the following comments, although UK-centered, have a wider resonance. Miners died prematurely in Britain from accidents, lung disease, and hard work under appalling conditions. The typical annual death rate in Britain was two per thousand. Miners' wages were forced down at times of depression by unscrupulous, inhumane, and even cash-strapped mineowners, the most notable case being the general strike of 1926. The miners held out for six months after the main strike had been broken but were forced eventually to accept longer hours and lower pay. The father of one of us (BGR) ran a concert party around Durham to raise money for the starving miners and their families. Winston Churchill, as Chancellor of the Exchequer, broke the strike ruthlessly, and was never a name to conjure with in coal-mining territory, whatever his reputation elsewhere.

Miners everywhere tend to live in isolated communities. Again, Britain is typical. Partly self-regulating, cleaving to their own traditions, music, and poetry, the miners stood apart and worked unseen. British coal lies in narrow seams deeply buried. They are uncomfortable and dangerous to work. Miners were seen as hardy and noble, hacking at the rock face, toiling in a dripping subterranean world where man was not meant to be. The jobs were inherited, passing from father to son; daughters married within the coal community.

George Orwell wrote "You and I owe the comparative decency of our lives to the brave, valiant souls underground, blackened to the eyes, with their throats full of dust." Mechanization of mining and better safety standards have improved the miner's lot from what it was in the nineteenth century and even since Orwell wrote, but the situation is far from ideal.

Meanwhile, demand for coal declined after World War II. Oil and natural gas replaced it in many applications. Coal is polluting, and European Commission legislation on air pollution discriminated against relatively high sulfur British coal for electricity generation, its major use in the United States. The possibility of imports of cheap strip-mined coal (much of it produced, say the miners, by sweated child labor in Columbia) has made things worse. The collapse of the British coal

industry led to the disappearance of employment – only 10,000 miners remain – the fragmentation of historic communities, and the depopulation of whole areas of the country.¹

Given the hardships of being a miner, the virtual disappearance of the UK coal industry at the end of the 1970s should have been an occasion for rejoicing. But reaction to the closure of the pits was ambivalent. It destroyed villages that offered no other employment. Mining was “a man’s job.” Miners saw themselves as the elite of manual workers. They lived in close-knit communities with a local culture. There were choirs, whippet racing, pigeon fancying, churches (usually Wesleyan Methodist), rugby league football, Pitman Painters, and village pubs. Should one applaud the ending of an unpleasant and dangerous industry or mourn the disappearance of employment and community?

In spite of the fate of the British industry, coal mining continues in many other countries, either where coal is more accessible or where the miners have little choice but to tolerate the underground work. The almost miraculous rescue of 33 miners in Chile, who had been trapped underground for two months from October 2010, and the 29 deaths in New Zealand in November 2010 underline both the solidarity of the mining communities and the dangers of their work.

Since 2004 coal has been the world’s fastest growing primary energy source. China accounts for 85% and it is the major energy source. Is coal so dangerous and polluting that it should be phased out? Can it be made less polluting both in terms of air pollution and its contribution to the atmospheric carbon dioxide levels? Can it be mined at lower social cost? These issues remain unresolved.

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CHAPTER 15

Fats and Oils

Naturally occurring triglycerides, that is, esters of glycerol with saturated or unsaturated fatty acids, are called oils if they are liquid or fats if they are solid.¹ They may be of animal or vegetable origin. They have the general formula: $\text{ROOCCH}_2\text{--CH(OCO R')--CH}_2\text{OOCR''}$, where R, R', and R'' are alkyl or alkenyl groups. Usually more than one fatty acid is present and the triglyceride is said to be "mixed." Some of the fatty acids most commonly found in triglycerides in fats and oils are shown in Table 15.1. They all have even numbers of carbon atoms.

Fats and oils are one of the three major groups of foodstuffs, the others being proteins and carbohydrates. Food, however, is surrounded with a host of cultural attitudes. In southern Europe, oil is widely used for cooking, whereas in northern Europe, solid fats have traditionally been preferred. In the Middle East, a market for butter scarcely exists, whereas in Europe and North America it is an important foodstuff. Therefore ways have been sought by which oils could be hardened to make them culturally acceptable to dwellers in northerly areas. The melting point of a fat or oil is related to the melting points of the fatty acids it contains, and these in turn depend on molecular weight (illustrated by the series lauric, myristic, palmitic, stearic), number of double bonds (illustrated by the series stearic, oleic, linoleic, linolenic), and the *cis* or *trans* configuration of the double bond (illustrated by the series linolenic, α -eleostearic, β -eleostearic). Crystalline structure of the fat also plays a part. To harden a fat or oil, therefore, it is hydrogenated over a nickel catalyst. In partial hydrogenation, *cis* double bonds may isomerize to *trans* double bonds. The degree of hardness can be controlled, and fats of any desired consistency can be produced.

The role of fats and oils in cardiovascular disease has been a major area of concern in recent years. European and North American diets are said to be too rich in fats and oils. Saturated fats and fats with *trans* double bonds have been associated with atheroma, and a switch to soft fats containing polyunsaturated side chains has been recommended. Thus a historic trend toward hard fats has been reversed. Opinion now seems to be stressing the virtues of monounsaturated fats whose fatty acid component is largely oleic acid. Also of interest are so-called omega acids. These acids have a

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TABLE 15.1 Common Fatty Acids

Formula	Trivial Name	Melting Point (°C)	Double-Bond Position and Stereochemistry	Source
$n\text{-C}_{11}\text{H}_{22}\text{COOH}$	Lauric acid	44.2		Coconut oil, palm kernel oil
$n\text{-C}_{13}\text{H}_{26}\text{COOH}$	Myristic acid	53.9		Coconut oil, palm kernel oil
$n\text{-C}_{15}\text{H}_{31}\text{COOH}$	Palmitic acid	63.1		Most vegetable oils and animal fats
$n\text{-C}_{17}\text{H}_{33}\text{COOH}$	Stearic acid	69.6		Most vegetable oils and animal fats
$n\text{-C}_{17}\text{H}_{33}\text{COOH}$	Oleic acid ^a	16.0	<i>cis</i> -9	Most vegetable oils and animal fats
$n\text{-C}_{17}\text{H}_{31}\text{COOH}$	Linoleic acid ^a	-9.5	<i>cis</i> -9, <i>cis</i> -12	(olives, nuts, beans, tall oil) Tall oil, most vegetable oils (safflower, sunflower, soy)
$n\text{-C}_{17}\text{H}_{29}\text{COOH}$	α -Linolenic acid ^b	-11.3	<i>cis</i> -9, <i>cis</i> -12, <i>cis</i> -15	Linseed oil
$n\text{-C}_{17}\text{H}_{29}\text{COOH}$	γ -Linolenic acid		<i>cis</i> -6, <i>cis</i> -9, <i>cis</i> -12	Evening primrose oil
$n\text{-C}_{17}\text{H}_{29}\text{COOH}$	α -Eleostearic acid	48.5	<i>cis</i> -9, <i>trans</i> -11, <i>trans</i> -13	Tung oil
$n\text{-C}_{17}\text{H}_{29}\text{COOH}$	β -Eleostearic acid	71.5	<i>trans</i> -9, <i>trans</i> -11, <i>trans</i> -13	Tung oil
$n\text{-C}_{17}\text{H}_{32}\text{O}_2\text{COOH}$	Ricinoleic acid ^a	5.0	<i>cis</i> -9	Castor oil
$n\text{-C}_{19}\text{H}_{37}\text{COOH}$	Eicosapentaenoic acid		<i>cis</i> -5, <i>cis</i> -8, <i>cis</i> -11, <i>cis</i> -14, <i>cis</i> -17	Fish oil
$n\text{-C}_{19}\text{H}_{37}\text{COOH}$	Arachidonic acid	-49.5	<i>cis</i> -5, <i>cis</i> -8, <i>cis</i> -11, <i>cis</i> -14	Animal fats and organs
$n\text{-C}_{21}\text{H}_{41}\text{COOH}$	Erucic acid	33.5	<i>cis</i> -13	Rapeseed (canola) oil
$n\text{-C}_{21}\text{H}_{39}\text{COOH}$	Docosahexaenoic acid	22.6	<i>cis</i> -4, <i>cis</i> -7, <i>cis</i> -10, <i>cis</i> -13, <i>cis</i> -16, <i>cis</i> -19	Fish oil

^a Oleic acid: $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$; linoleic acid: $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$; linolenic acid: $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_5\text{COOH}$; ricinoleic acid: $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$.

final carbon–carbon double bond in the ω -3 position, that is, the third bond from the methyl end of the fatty acid.

15.1 MARKETS FOR FATS AND OILS

World production of fats and oils in 2008 was 128 million metric tons (282 billion pounds). The U.S. consumption was about 12.2 million metric tons (26.9 billion pounds – about 105 pounds per person). This figure is similar to the production of propylene or benzene. The difference is that propylene and benzene are almost entirely used by the chemical industry whereas 88% of oils and fats are eaten by humans and another 6% of poorer grade material is made into animal feed. The remaining 6% – about 1.6 billion pounds – is used by the oleochemical industry. That is about the same as caprolactam production and a bit greater than *ortho*-xylene production. Thus, in volume terms, oleochemicals are comparable to one fraction of one of the seven major building blocks.

Figure 15.1 shows world production of the different oils and fats. Four oil crops – soybean, palm, rape, and sunflower – have grown rapidly over the past 35 years compared with traditional oils and fats. They have gone from 26% of world production between 1958 and 1962 to 83% in 2009. The fastest growing has been palm oil because of excellent merchandising primarily by Malaysia and Indonesia.

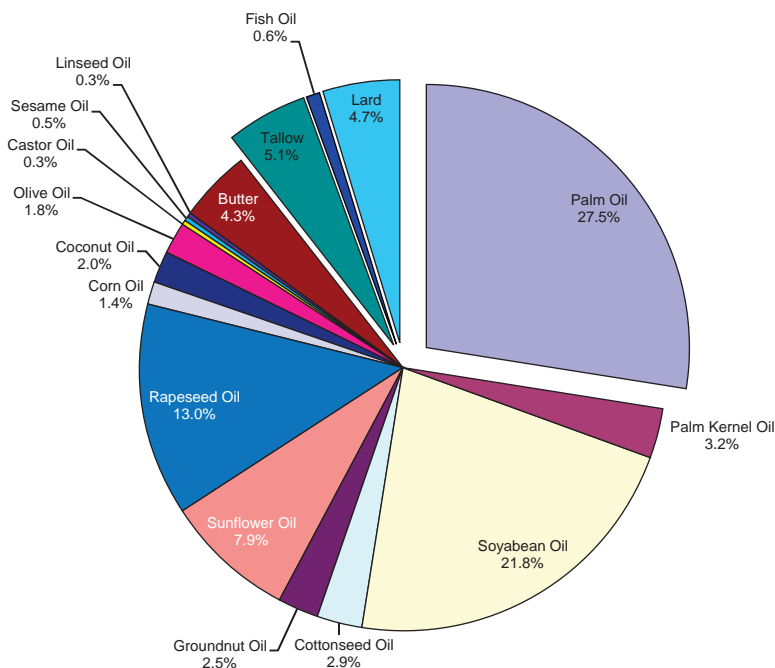


FIGURE 15.1 World production of fats and oils (2009).

Also, palm oil yields are about 4000 kg/hectare (3570 pounds/acre) compared with 875 kg/hectare (781 pounds/acre) for peanuts, 675 (273) for rapeseed, 355 (317) for coconuts, and 350 (312) for soybeans. Animal fats have only a relatively small market – less than a fifth of the size of the oils market, made up of tallow, lard, and butter in very approximately equal amounts. Production has been static for about 40 years.

Oil-producing countries specialize to some extent. Malaysia grows mainly palm oil and is responsible for 51% of world production. The Philippines grows 43% of the world's coconut oil. Rapeseed or canola oil production is divided between China (27%), Europe (25%), India (19%), and Canada (15%) leaving 14% for “others.” Russia (25%), Europe (20%), and Argentina (16%) are the major sunflower oil producers, while the United States has 56% of soybean oil production and Argentina another 22%. The United States, China, and the CIS dominate the cottonseed market. The Philippines dominates the coconut oil business because they trained workers to climb the telephone pole-like palm trees and harvest the coconuts at the top of the tree. Later the workers trained monkeys to do the same thing.

Rapeseed oil containing 90% erucic acid is a new development as is a sunflower oil with 80% oleic acid. Rapeseed as a source of oil is important not only because the oil has a high concentration of unsaturated fatty acids, but also because it can be grown in colder climates than other oilseeds. Thus it is an important crop in Canada and northern Europe. Its importance in Europe, however, reflects the desire of the European Commission to support European farmers and replace imports. It provides little if any economic advantage. At February 2003 prices, the production cost of palm oil produced in Malaysia and delivered to the United States was \$698/metric ton. Soybean oil in the United States cost \$489/metric ton and rapeseed oil in Europe \$750/metric ton. The original rapeseed oil contained 40–50% erucic acid, a C_{22} fatty acid with a single double bond, together with so-called glucosinolates, which are toxic compounds inhibiting growth by blocking the capture of iodine by the thyroid gland. Animals (rats, guinea pigs, ducklings, hamsters) fed on a high erucic acid diet concentrated fat in the heart muscle. While there is no evidence that erucic acid has a similar effect on humans, the oil market is geared to edible oils. The Canadians thought it prudent to remove or breed out the glucosinolates. Thus there was developed a zero erucic acid rapeseed, which they called canola oil, the name coming from CANada OiL. Some high erucic acid oil is still required for industrial needs, and thus a high erucic acid crop is also grown. It is important to prevent cross pollination of one crop by the other. Rapeseed oil goes into lubricants for diesel engines and erucic acid amide is used as a lubricant in plastics extrusion.

Although fats and oils are produced worldwide, the industrial chemistry associated with them has largely been limited to the United States and Europe. In 2010, however, Saudi Arabia's SABIC announced an oleochemicals plant to come on stream in 2013 that will produce fatty acids, fatty alcohols, and glycerol. SABIC is thus expanding its chemical business into downstream and specialty chemicals.

The U.S. consumption of fats and oils is shown in Table 15.2. The most important fat or oil in the United States is soybean oil of which about 8.82 million metric tons (19 billion pounds) was produced in 2008. The chemical industry obtains most of its

TABLE 15.2 Selected Fats and Oils Consumed in End Products: United States 2008 (millions of pounds)

	Total All Products	Edible Products	Inedible Products
Total fats and oils	35,231.0	22,662.2	12,568.8
Castor oil	117.7	0.0	117.7
Coconut oil	778.7	377.7	401.0
Corn oil	NA	1,773.3	NA
Cottonseed oil	NA	793.4	NA
Edible tallow	751.2	161.6	589.5
Inedible tallow and grease	3,863.6	NA	3,863.6
Lard	483.7	182.0	301.7
Linseed oil	75.8	NA	75.8
Palm oil	NA	848.9	NA
Palm kernel oil	374.8	374.8	NA
Rapeseed oil	2,747.1	1,914.6	832.5
Soybean oil	19,449.6	15,724.9	3,724.7
Tall oil	1,644.4	NA	1,644.4
Vegetable foots	68.4	NA	68.4
Other fats and oils	4,876.0	511.0	1,067.2

Note: NA = not available. Data include hydrogenated fats (vegetable and animal) and other fats and oils in process. Other fats and oils include corn oil, fish oil, peanut oil, tung oil, and safflower oil.

fatty acids (palmitic, stearic, and oleic) from lower grade oils or animal fats. The sources of fatty acids for the chemical industry are shown in the final column of Table 15.1.

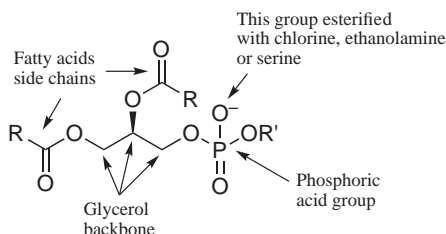
15.2 PURIFICATION OF FATS AND OILS

Inedible beef tallow is a major item in Table 15.2. Tallow is extracted from the fatty animal tissues in slaughterhouse wastes by rendering. In “dry” rendering, heat alone is used to dry the material and liberate the fat. In “wet” rendering, the fat is liberated by hot water or steam, which is then separated by skimming or centrifuging.

Oils are extracted either by pressing (“expression”) or by solvent extraction. Expression, for example, of peanuts, formerly left about 6% of the oil in the so-called oil cake, but modern presses leave only 3–5%. Nonetheless, solvent extraction may be preferred because it leaves less than 1%. Soybean oil is invariably solvent extracted, usually with hexane. The soybeans are heat-treated and then mechanically pressed to flakes. The flakes are solvent extracted (leached) with hexane, which is subsequently stripped off and recycled.

A modern trend is the use of supercritical carbon dioxide for solvent extraction of oils for food and personal products. For example, it is used for high cost products such as decaffeinated coffee and essential oils for the perfume industry. It was suggested as an attractive process for edible oils because it would avoid the traces of hexane contamination, but thus far the expense of the capital equipment has deterred the industry.

Once the oil has been extracted, it is subjected to a series of purification processes: degumming, refining, bleaching,² deodorization, and possibly fractionation by melting point. Hydrogenation is an important chemical modification. In the degumming process, phospholipids are removed by washing the oil with hot water or dilute acid. The phospholipids precipitate and are removed as a sludge and vacuum dried. Alternatively, they are removed during the alkali refining treatment. The sludge contains four major constituents, which are esters of phosphatidic acid. These are 1,2-diglycerides with a phosphoric acid group on the third carbon, and the phosphoric acid group is in turn esterified with the hydroxyl group of choline, ethanolamine, or serine. If the structure is written



and $R = \text{stearic, palmitic, or oleic}$, then if $R' = \text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2$, the compound is called lecithin or phosphatidylcholine; if $R' = \text{CH}_2\text{CH}_2\text{NH}_2$, it is cephalin or phosphatidylethanolamine; and if $R' = \text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, it is phosphatidylserine. The trade lecithin, although predominantly phosphatidylcholine, is a mixture of all three plus minor components. It is used as a cationic surfactant in foods and specialty chemicals. For example, it is added to chocolate and soft margarine. In chocolate it prevents the “blooming” or precipitation of minute fat particles that give the chocolate a grayish cast. There is some clinical evidence that phosphatidylserine enhances memory in elderly persons suffering from memory loss.

Vegetable oils usually contain free fatty acids resulting from enzymatic decomposition. If the oils are to be used as foodstuffs, these are removed by alkali treatment in a so-called refining process. The sodium salts of the fatty acids are separated. They are called soapstocks or “foots.” The free fatty acids are regenerated by acidification. Associated with them are small quantities of tocopherols, which may be converted to vitamin E, and small amounts of sterols, including stigmasterol, which can be converted to cortisone. Stigmasterol is one of the few naturally occurring sterols with an unsaturated side chain. The double bond makes possible side chain cleavage and, with subsequent chemical reactions, transformation to progesterone. This in turn is converted to cortisone. A key step is the enzymatic insertion of oxygen in the 11-position.³ The major source of tocopherols and sterols is the deodorizer distillates mentioned below.

The bleaching process decolorizes the oil by adsorption rather than by oxidation, which is the mode of action of conventional bleaches. The colored material is adsorbed on bentonite or montmorillonite clays. The oil may then be fractionated by melting point to extract a particular range of triglycerides, or it may be hydrogenated.

Hydrogenation is carried out over a nickel catalyst and “hardens” the oil; that is, it raises the melting point. Margarine is a typical product. The hardening process involves reduction of double bonds, *cis*–*trans* isomerization, and shifting of double bonds along the chain. A problem is that the resulting *trans* fatty acids, when eaten, appear to increase total levels of blood cholesterol and LDL cholesterol, while reducing HDL cholesterol (the good one). *trans* Fatty acids are also associated with Alzheimer’s disease, diabetes, and obesity, although correlations are less well established. This problem and the efforts to solve it are discussed in Section 15.12.2.

Deodorization involves removal of the strong flavor associated with vegetable oils. It depends on a combination of high vacuum (0.004–0.008 bar) and high temperature (240–260°C) for 15–40 minutes and is a variant of vacuum steam distillation, which removes undesirable volatiles while not damaging the triglycerides. A distillate results (deodorizer distillate) containing odor bodies together with small amounts of two valuable products. One is a mixture of tocopherols, the precursor of vitamin E and thus the source of natural vitamin E. The other is a sterol mixture containing stigmaterol and sitosterols. Stigmaterol is the major raw material in the United States for cortisone.

15.3 FATTY ACIDS

Worldwide, fatty acid production by hydrolysis of natural fats and oils was 4 million metric tons in 2007.⁴ That means that about 3% of total fats and oils is further processed in this way. They are saponified to glycerol and soap, the sodium salt of fatty acids, by treatment with alkali (Fig. 15.2) when soap is the desired end product. More

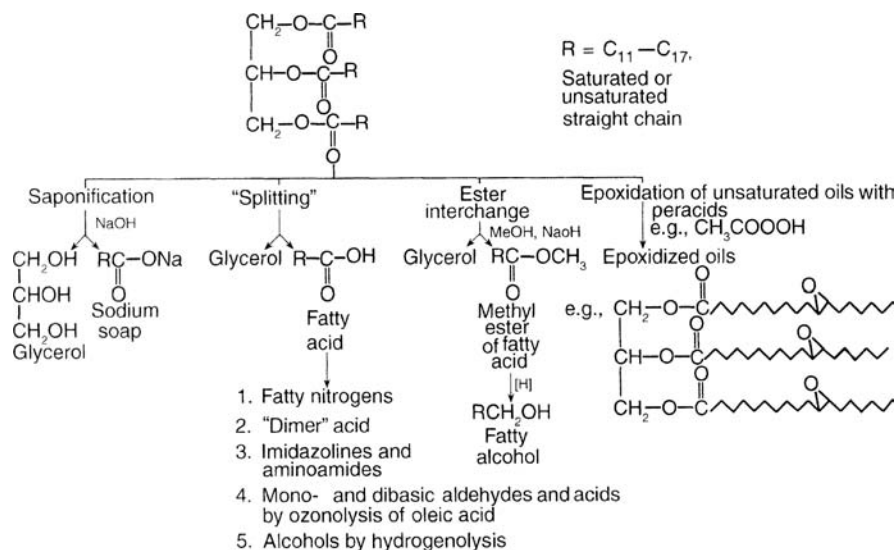


FIGURE 15.2 Chemical reactions of fats and oils.

widely used in both the United States and Europe to obtain free fatty acids is “splitting” – continuous noncatalytic hydrolysis at high temperature and pressure. In smaller plants, continuous autoclave splitting is used in the presence of oxide catalysts such as zinc oxide, and very small operations may use batch processes with so-called Twitchell catalysts, which are combinations of sulfuric and sulfonic acids.

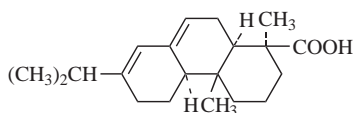
The separation of saturated from unsaturated acids, if required, is normally effected by cumbersome crystallizations. A somewhat less efficient but simpler process for separating fatty acids, primarily from tallow, is known as hydrophilization. An aqueous solution of a wetting agent is made into a slurry with a crystallized fatty acid mixture. The higher melting stearic acid crystals are wetted preferentially and are sufficiently solubilized by the wetting agent to transfer into the aqueous phase. The aqueous layer is separated from the oleic acid by centrifugation. Heating melts the stearic acid, which separates from the water and is easily isolated.

The enzymatic hydrolysis of fats has been studied extensively but a practical process that proceeds at an acceptable rate has not yet been devised. Another source of the vegetable oil fatty acids used by the chemical industry is “foots” or soapstocks (see above).

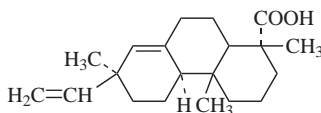
The lower molecular weight acids, lauric and myristic, come from coconut and palm kernel oils. Palmitic and stearic acids are found in most oils and fats, tallow being the most important. Oleic acid is a component of animal fats and a major constituent of many vegetable oils such as olive oil. Its ozonolysis gives azelaic and pelargonic acids (Section 15.7). 12-Hydroxyoleic (ricinoleic acid) with its hydroxyl group is an oddity found in castor oil. Erucic acid (see above) is found in rapeseed oil from plants where it has not been removed by breeding.

Linoleic acid is found in many vegetable oils, particularly linseed and safflower oil. Nonetheless, it is largely obtained from tall oil, which became important after World War II. Tall *oil* is a misnomer, because oils are triglycerides by definition, and tall oil is a mixture of rosin and fatty acids. It is a by-product of the pulping of southern pine for paper manufacture. Southern pine is converted to pulp by the Kraft process, in which sodium hydroxide is used to separate the desired cellulosic fibers from the undesired lignins (polymers of phenylpropane monomers containing OH and OCH₃ groups), rosins, fatty acids, and other materials in the wood. The fatty acids, mainly oleic and linoleic, end up as their sodium salts in a smelly black liquid. Acidification gives rosin and fatty acids (mainly oleic and linoleic) which may be separated by distillation.

Rosin is a complex mixture of about 90% acids, related to partially hydrogenated phenanthrene, and 10% neutral matter. Of the rosin acids, 90%, including pimaric acid, are isomeric with abietic acid and the remainder with dihydro- and dehydroabietic acids, in which one or both double bonds have been reduced.



Abietic acid



Pimaric acid

Rosin is famous for its use on violin bows, but far larger quantities are formulated into paints and varnishes. As its sodium salt, it is the important size in paper manufacture, and this is its major use.

The fatty acids with more than 18 carbon atoms are found in fish oils. They are of current interest because arachidonic acid, 5,8,11,14-eicosatetraenoic acid, has been shown to be the progenitor of the prostaglandins, remarkable chemicals with multiple physiological functions that occur in minute quantities in the body. It reacts in the body to give prostaglandins, leukotrienes, thromboxanes, and prostacyclins. They are “essential” in that they cannot be synthesized by the body and must be obtained in diet.

Evening primrose oil is advertised as being rich in the important C₁₈ fatty acid, γ -linolenic acid, an isomer of the α -linolenic acid from tall oil. The seeds of the evening primrose fall when ripe, that is, over a long period. As a result, commercial harvesting gives only about 5% recovery. This makes it impossibly expensive. Fortunately, the active ingredient can be manufactured by fermentation using fungi of the class *Phycomycetes*. For example, species of *Mucor* can be grown on a glucose-containing medium in large fermenters (about 220 m³), and an oil containing 7% γ -linolenic acid can be recovered from the fungal mycelium. Another useful species is *Phycomyces blakesleeanus*, its oil also containing large quantities of β -carotene.

In Russia, Japan, and China, impure petrochemical-based fatty acids with mixtures of odd and even numbers of carbon atoms have been produced by oxidation of petroleum wax. The products are generally regarded as inferior.

15.3.1 Applications of Fatty Acids

A large proportion of fatty acid production goes into soaps. Domestic soap is merely the sodium salt of the mixture of fatty acids obtained by hydrolysis of fats or oils. In practice, the fat or triglyceride is treated with sodium hydroxide to yield the sodium salt (or soap) and glycerol. The process is called saponification. The major components are sodium stearate and palmitate. Soap is also used as a lubricant in rubber and polymer processing.

The reaction of soap with hydrochloric acid to yield sodium chloride and a fatty acid mixture called stearine was discovered in 1823 by Chevreul, who became well known because he lived to be over 100 years old. In the nineteenth century, until the advent of cheap paraffin wax, it was the principal material used in household candles. Unlike the traditional tallow, it did not give acrolein, a powerful lachrymator, on combustion. It is still blended with paraffin wax in some candle formulations to improve the melting properties of the wax. Only in countries such as Denmark and Sweden, whose fishing industries produce a surplus of cheap stearine, is it still a major component of candles. Paraffin candles dominate the world market, which has passed its nadir and is again growing. This is partly due to fashion in developed countries but also to the frequent interruptions in electricity supply in developing countries, where the inhabitants are no longer content to sit in the dark. Paraffin wax comes from the heavier petroleum fractions; ceresin or microcrystalline waxes from the same source are used in U.S. candles. These are branched chain paraffins and consequently must be blended with an antioxidant to prevent oxidation at the tertiary carbon atoms.

Fischer–Tropsch waxes are made in South Africa (Section 14.2) and in Shell’s Middle Distillate Synthesis (Section 12.7.2). They are probably the reason why Shell’s process is profitable. The waxes of higher molecular weight are used throughout the world for the fashionable long, thin candles, while the fraction equivalent to paraffin wax is used in the larger domestic market.

Salts of fatty acids are used as stabilizers for poly(vinyl chloride). These are the laureates or stearate of metals such as lead, barium, calcium, strontium, and zinc. Metal salts of cobalt, lead, manganese, calcium, and zirconium can be added to unsaturated oils to accelerate their oxidation and are thus used as so-called driers in oil-based paints. Metal soaps, for example, those based on lithium, are also used to thicken lubricating oils to yield greases. Free fatty acids may be components of automobile lubricating oil formulations. The sucrose esters of fatty acids are said to have advantages such as biodegradability and nontoxicity over traditional oils and fats, particularly in lubricant and food formulations (Section 16.1). Microbial conversion of fatty acids gives mono-, di-, and trihydroxy derivatives that are said to have antimicrobial, medical, and industrial properties, but applications are still in the exploratory stage.

15.4 FATTY NITROGEN COMPOUNDS

Fatty acids may be converted into a large number of fatty nitrogen compounds of which the fatty amines, including quaternary amines, are the most important. Some of these are shown in Figure 15.3. They find many applications in industry as surface active agents. The worldwide market for fatty amines in the early 2000s was about 600,000 metric tons with the United States consuming about a third of this.

In Figure 15.3, the route to fatty nitrogen compounds starts with fatty acids in which the alkyl group may contain 7–17 carbon atoms. Normally it is saturated, although derivatives based on oleic and erucic acids are also produced. Treatment with ammonia converts the fatty acid to a nitrile through successive dehydrations of the ammonium salt and the amide, neither of which need be isolated. This chemistry was observed earlier in the classic synthesis of hexamethylenediamine (Section 7.1.5). Amides, however, are articles of commerce and are used as a parting agent or slip agent to prevent plastic from adhering to the die during extrusion. The nitrile in turn may be reduced to a primary, secondary, or tertiary amine. Conditions for primary amine formation require that ammonia be present to suppress secondary amine formation. Conversely, when the secondary amine is the desired product, ammonia must be removed continuously from the reaction mixture. The tertiary amine may also be prepared by hydrogenation with removal of ammonia. It is better prepared, however, by the interaction of a diamine with an alcohol. The primary, secondary, and tertiary amines may be quaternized with methyl chloride or sulfate.

The most important use for distearyldimethylammonium chloride is as a textile softener for home laundering. It must be added during the last rinse, otherwise it will

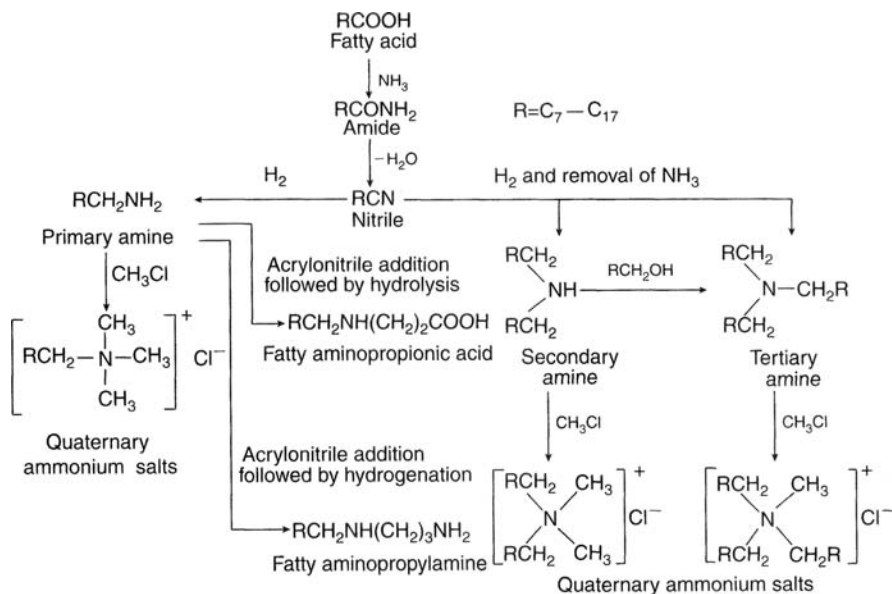


FIGURE 15.3 Fatty nitrogen chemistry.

precipitate on contact with anionic detergents. Although still widely used, it is believed to present some ecological problems. Substitutes are certain ethoxylates (Section 5.7) which are nonionic and can be included as part of the detergent formulation.

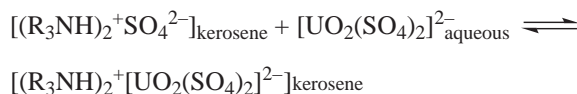
Distearyldimethylammonium chloride and related quaternaries also react with bentonite clays to modify them, so that they are dispersible in organic solvents. As such they are the basis for high performance greases, which result when the organoclay is dispersed in mineral oil. These organoclays are also used in oil-based paints to impart thixotropy.

An application for long chain quaternary alkylammonium compounds is in phase-transfer catalysis (Section 18.10). A related application is liquid ion exchange used primarily in the extraction of uranium from its ore. The uranium ore is leached with sulfuric acid to give the complex anion $[\text{UO}_2(\text{SO}_4)_2]^{2-}$. A trifatty amine in which the fatty groups contain 8–10 carbon atoms is converted to a sulfate as shown in equation 1 and this organic-soluble salt, dissolved in kerosene, is mixed with the aqueous leach liquor containing the uranium anion. On vigorous stirring, ion exchange takes place between the sulfate ion of the trifatty amine salt and the uranium-containing anion so that the latter is transferred to the organic solution whereas the sulfate is transferred to the aqueous layer (equation 2). Thus the uranium, which was present in the aqueous phase at a concentration of considerably less than 1%, is not only concentrated in the organic phase but is separated from numerous impurities. It can be removed from the organic phase by stripping with an alkali (equation 3), which converts it into “yellow cake.” The trifatty amine is recycled.

1. Salt formation:



2. Liquid ion exchange:



3. Stripping:

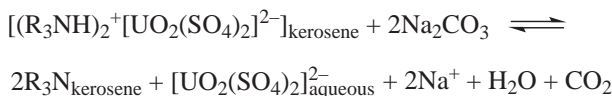


Figure 15.3 shows another reaction sequence for primary amines. They may react with acrylonitrile to give a fatty aminopropionitrile. This in turn can be reduced to a fatty aminopropylamine or hydrolyzed to a fatty aminopropionic acid. Each of these compounds varies in degree of surface activity, and it is this variation that accounts for their specific applications. For example, the diamine is used as a corrosion inhibitor, and the amino acid is an amphoteric detergent.

In addition to the foregoing simple reactions, fatty acids undergo a number of more complicated reactions of chemical interest, although the tonnages involved are small compared with petroleum and natural gas derivatives. Many of the products, however, are not accessible from petrochemical sources. An example is “dimer acid.”

15.5 “DIMER” ACID

The dimerization of linoleic acid is shown in Figure 15.4a. Natural linoleic acid has double bonds in the 9,12 positions (Table 15.1) but, when heated, it isomerizes to the more stable conjugated 10,12 or 9,11 structures. In Figure 15.4a, the 9,11 acid is shown. This diene may then undergo a Diels–Alder reaction with another molecule of the original 9,12 acid or either of the conjugated isomers. The figure shows the reaction with the 9,12 acid to give a typical Diels–Alder adduct – a cyclohexane with four side chains, two of which contain carboxyl groups.

The conjugation reaction can go in two ways, and the products can react with either of the double bonds in the 9,12, 10,12, or 9,11 acids. Furthermore, addition may be head-to-head or head-to-tail. The figure shows head-to-head addition. In all, 24 different products are possible. An added complication is that the double bonds can be *cis* or *trans*. Although most naturally occurring double bonds, including those in linoleic acid, are *cis*, some *trans* double bonds form at the temperature of the reaction. Whether they are *cis* or *trans*, however, markedly affects the kinetics of the reaction.

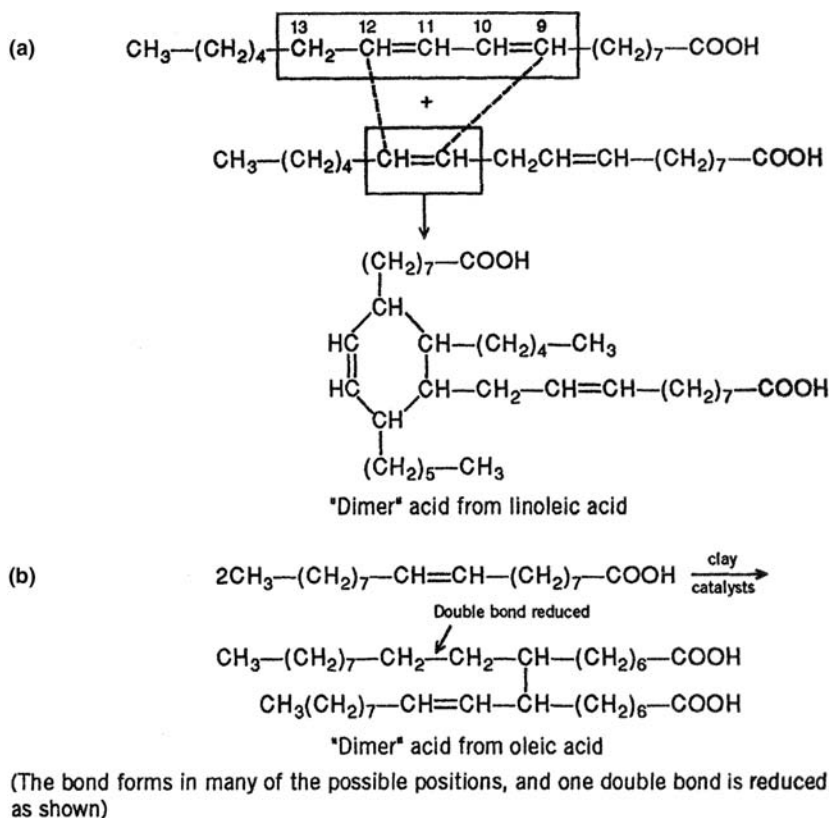


FIGURE 15.4 "Dimer" acid.

Linoleic acid is scarcer and more expensive than oleic acid, and it was desirable to find a way to dimerize the cheaper oleic acid, which, with its single double bond, will not undergo the Diels–Alder reaction. It will, however, dimerize over a natural acid clay catalyst, for example, a montmorillonite, known as a “pillared clay.” Such a clay consists of layers separated by ions, such as metal ions, which function as “pillars.” Large organic molecules can undergo reactions in the spaces between the layers. Oleic acid dimerizes as shown in Figure 15.4b. This is one of the relatively rare examples in organic chemistry of an intermolecular dehydrogenation. For it to proceed, the hydrogen must react immediately when it is produced, and here it hydrogenates the double bond. Other examples are benzene/ammonia (Section 9.3) and methane/ammonia (Section 12.1).

The product from oleic acid is also known as “dimer acid,” and many different chemical structures are present, although all contain 36 carbon atoms and two carboxyl groups. The U.S. demand in 2009 was about 55,000 metric tons. These dibasic acids are used in the production of specialty polyamide oligomers (“Versamids”) with unusual adhesive and coating properties. For example, when reacted with ethylene diamine, an alcohol-soluble oligomer results that adheres to

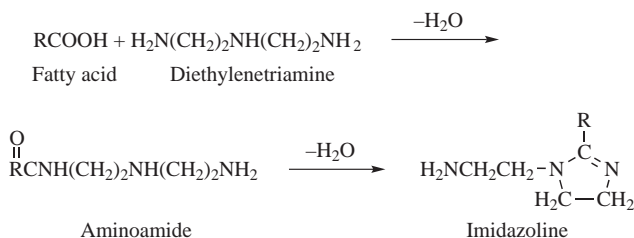
polyethylene, and which is therefore useful as a vehicle for printing inks for polyethylene film. The alcohol solubility is necessary since stronger solvents such as aromatic hydrocarbons dissolve the natural rubber flexographic printing rolls.

When dimer acid reacts with diethylenetriamine, triethylenetetramine, or higher polyalkylene amines, an amino-containing polyamide oligomer results. It is an important coreactant for epoxy resins for adhesives and particularly for maintenance paint for metals. The amino-containing resin imparts corrosion resistance by reacting chemically with the metal oxide surface (e.g., ferric oxide) that is invariably the top layer of iron exposed to air. The chemical reaction is salt formation that takes place between the acidic hydrated amine groups and the basic hydrated metal oxides.

An interesting specialty use involves the substitution of dimer acid esters, such as the di-(2-ethylhexyl) ester, for lubricating oil in two-cycle outboard engines in lakes in Switzerland that were being polluted by petroleum engine oil discharged from motor boats.

15.6 AMINOAMIDES AND IMIDAZOLINES

A small volume application of fatty acids involves their conversion to aminoamides and imidazolines. In some applications such as flotation and corrosion inhibition, they compete with the fatty nitrogen compounds discussed in Section 15.4. A fatty acid will react with a polyamine such as diethylenetriamine to give an aminoamide, a molecule of water being eliminated. Further dehydration leads to cyclization. Imidazolines have many of the properties of the fatty nitrogen compounds already described.

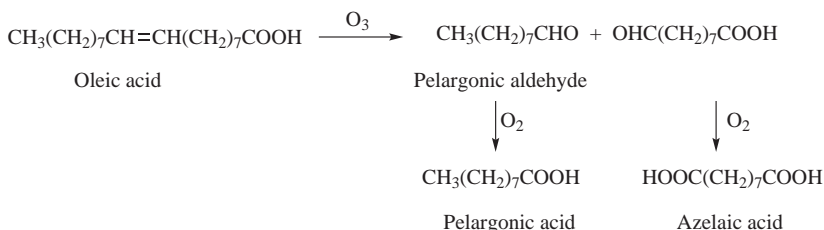


If quaternized with methyl chloride or sulfate, they are useful as textile softeners, like the fatty quaternaries already discussed (Section 15.4). Their main use is as corrosion inhibitors, particularly in petroleum applications. They are also used as asphalt emulsifiers and antistrippers. An asphalt emulsifier is an emulsifying agent that brings particles of liquid asphalt and water into close proximity to provide a convenient means for laying down a layer of asphalt on a road bed. An asphalt antistripper causes asphalt to adhere to the rock or aggregate with which it is frequently mixed in road construction. The antistripper is particularly useful if the road is wet. It functions by adsorbing onto the surface of the rock, which is usually silica. Adsorption is so strong that water on the surface of the rock is replaced.

The fatty tails point away from the surface of the rock and are solvated by the asphalt. In this way, aminoamides and imidazolines facilitate the bonding between the asphalt and the rock.

15.7 AZELAIC, PELARGONIC, AND PETROSELINIC ACIDS

Oleic acid may be cleaved at the double bond by treatment with ozone from an electrical discharge. Intermediate aldehydes form that can be oxidized to acids in situ.

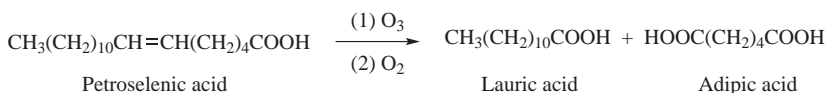


A petrochemical-based pelargonic acid process has been developed by Celanese, and thus once more petrochemicals have encroached on natural products. The Celanese process involves the linear hydroformylation of 1-octene, followed by oxidation of the resulting aldehyde (Section 6.9.2).

Both azelaic and pelargonic acids are raw materials for specialty polymers and polyesters for synthetic lubricants. Thus a typical first generation synthetic automotive lubricant, useful at very low temperatures, is the diisodecyl or ditridecyl ester of azelaic acid. The pelargonic acid also finds its way into synthetic lubricants by way of pentaerythritol pelargonate (Section 5.11.3). However, most important today is the trimer of 1-decene (Section 5.3). A lubricant used in automobiles is actually a mixture of all three. In comparison with petroleum lubricants they are said to provide greater lubricity, better engine protection, and lower gasoline consumption. They are also easier to recycle. They may be blended with oil-derived hydrocarbons, which reduces the cost but increases the difficulty of recycling.

Odd number carbon atom acids are rare in nature and in industrial chemistry. Azelaic and pelargonic acids are the most accessible. It appears that odd number carbon acids are often more surface active than are those with an even number.

In an effort to find natural products to compete with petrochemicals, some effort is being invested in the production of seed oils from *umbelliferae*, for example coriander. Their seeds are rich in petroselinic acid, an isomer of oleic acid with a *cis*-6 double bond. Ozonolysis followed by oxidation gives adipic and lauric acids, products with larger markets than azelaic and pelargonic acids. Adipic acid is more readily available from petrochemical sources (Section 7.1.6.4) and lauric acid from coconut oil (Section 15.1)



15.8 FATTY ALCOHOLS

Fats and oils may easily be “split” to fatty acids and glycerol (Section 15.3). They can also be converted to fatty alcohols and glycerol by hydrogenolysis (see Fig. 15.2). Because the fatty acid groups have mixed chain lengths, a mixture of fatty alcohols results. The hydrogenolysis was originally carried out with sodium in ethanol – the Bouveault–Blanc reaction – but hydrogen and a copper chromite catalyst at high pressures are now used. The products differ in that the latter method hydrogenates all the double bonds in the fatty alcohol whereas the Bouveault–Blanc procedure leaves them intact. A proprietary chromite catalyst, however, is said to preserve the double bonds.

In practice it is easier to convert the fatty acid in the triglyceride to its methyl ester by alcoholysis with methanol, and then to subject the methyl ester to hydrogenolysis. Most vegetable-oil-based alcohols are made in this way.

While esters undergo hydrogenolysis to fatty alcohols fairly easily, reduction of a fatty acid to a fatty alcohol is more difficult. A clever procedure that brings it about involves a copper chromite catalyst (as above) in a slurry in fatty alcohol. The small amount of alcohol esterifies some of the fatty acid, the hydrogenolysis catalyst serving also as an esterification catalyst. The ester undergoes hydrogenolysis (Fig. 15.5) to yield a fatty alcohol which esterifies more of the fatty acid to yield an ester for further hydrogenolysis. Thus, even though the feed is fatty acid, an ester forms *in situ* for the hydrogenolysis. Since this is a high molecular weight ester, it reacts more slowly than a methyl ester, but the process is still useful industrially.

The hydrogenolysis of the fatty acids takes place at 250–300°C and 200–300 bar. Catalysts that cause lower molecular weight esters to undergo hydrogenolysis at considerably milder conditions such as 5–25 bar have been described recently (Section 5.7.2). Conceivably, modifications of these catalysts could be used for the hydrogenolysis of fatty acid esters under less strenuous conditions.

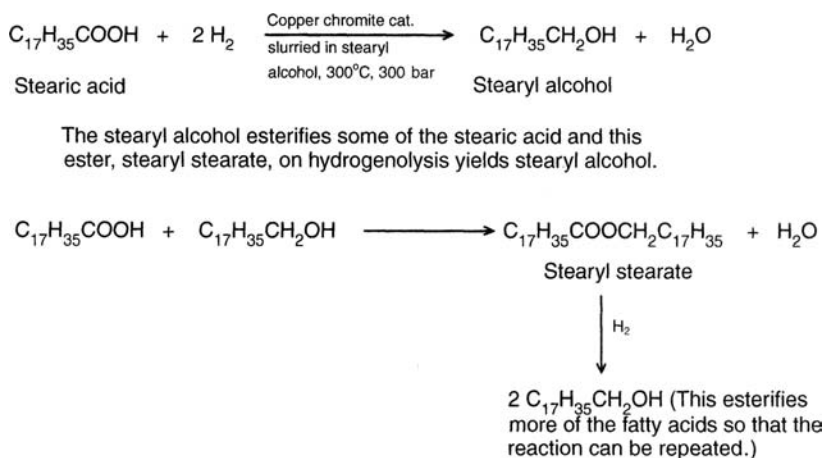


FIGURE 15.5 Hydrogenolysis of fatty acids.

Fatty alcohols as well as α -olefins may also be obtained from ethylene oligomerization by use of aluminum trialkyls (Section 5.3.2) or by the Shell SHOP process (Section 5.3.4). Here again petrochemicals have made an impact on traditional processes, but the vegetable-oil-based routes, used primarily by Henkel in Germany and Proctor & Gamble in the United States, are competitive, at least when vegetable oil prices are low. Together, the two processes accounted for 450,000 metric tons/year of alcohols in the United States in the early 2000s. Worldwide demand was about 750,000 metric tons.

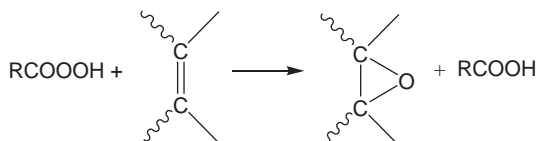
The possibility of using triglycerides directly in a hydrogenolysis reaction has long been discussed but never achieved commercially. The proposed catalyst is copper chromite in the form of lumps and the reaction has been run at 180–250°C at up to 280 bar.

The special role now occupied by straight chain primary alcohols in detergent technology results not only from the excellent detergent properties of their derivatives but also because products based on them biodegrade more quickly than compounds containing a benzene ring. Furthermore, degradation of benzene-ring-containing detergents eventually leads to phenols, and these are toxic to fish.

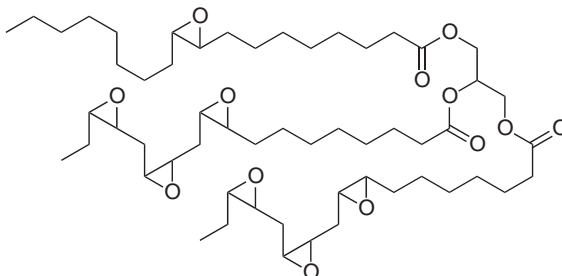
This has been hotly contested by the manufacturers of linear alkylbenzene sulfonates who, after all, are selling the most widely used surfactants in the world. Proctor & Gamble claim that linear alkylbenzene sulfonates are completely biodegradable aerobically, and can be completely biodegraded anaerobically as well, but only if oxygen is available initially to start the process.⁵

15.9 EPOXIDIZED OILS

Unsaturated fats and oils can be epoxidized so that some of the double bonds are replaced by epoxide groups. Peracids are frequently used:



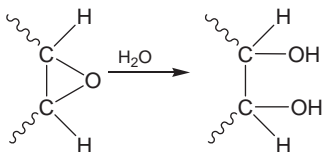
These compounds are added to poly(vinyl chloride) (PVC), often together with metal soaps, to prevent degradation by light and heat. The epoxidized oils stabilize PVC by mopping up free chlorine radicals that would otherwise cause the PVC chain to “unzip” in a free radical chain reaction. The structure of epoxidized soy oil is



Epoxidized oils are also secondary plasticizers; that is, they add their softening power to that of any plasticizer that softens PVC when used on its own. Epoxidation of fatty acid esters such as butyl or hexyl oleate or “tallate” gives a primary PVC plasticizer (Section 11.1.1). Such materials are widely used in the United States where soybean oil is produced on a large scale. In 2001, 70–80 thousand metric tons of epoxidized soya oils was produced in the United States, representing about 7.5% of total plasticizer production. In Western Europe, on the other hand, epoxidized oils are normally used only for their stabilizing properties, and consumption is much smaller.

A notable application for epoxidized oils is in the PVC gaskets for food products that are stored in glass jars with metal lids. They help to give an airtight seal, preventing contamination and preventing PVC deterioration during sterilization. Traces apparently migrate into the foodstuffs, and the extent and danger of the migration are currently being monitored.

Cargill has recently developed a group of “green” polyols by epoxidizing unsaturated vegetable oils and then hydrolyzing the epoxide groups at mild temperature and ambient pressure to give polyols.



These are used for several polyurethane applications, including flexible foams, which are the most technically challenging.

15.10 RICINOLEIC ACID

Ricinoleic acid, with its OH group, is found as its triglyceride only in castor oil. Well over 50,000 metric tons of castor oil is consumed yearly in the United States, the largest application being in paints and varnishes. Dehydration of the acid gives an isomer of linoleic acid that can be used in nonyellowing protective coating formulations. Castor oil itself may also be dehydrated to give a useful drying oil and it may be sulfated to give Turkey-Red oil, a textile dye leveler. It is also used as a polyol (3 hydroxyls per molecule of oil) in polyurethane production.

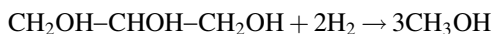


Undecylenic acid, as its zinc salt, is a fungicide effective against tinea pedis or athlete's foot.

15.11 GLYCEROL

We have already described the production of glycerol from fats and oils (Section 15.1) and from propylene by way of allyl chloride (Section 6.11.2). Its major uses are in the formulation of cosmetics, toiletries, foods, and beverages for its moisturizing, lubricating, and softening characteristics. It is also a humectant in tobacco and serves as a plasticizer for cellophane. The U.S. average annual production of glycerol between 2000 and 2004 was 350,000 metric tons. By 2010, the figure for the United States and Europe together was 950,000 metric tons. Production will increase as the EU directive 2003/30/EC is implemented, which requires the replacement of 5.75% of petroleum fuels with biofuels across all member states by 2010. It is projected that by the year 2020, production will be six times more than demand.

Because glycerol is a by-product of biodiesel manufacture (Section 15.12.3) it was already dramatically in surplus by 2008. Three hundred and fifty thousand metric tons was said to have been incinerated in the United States in that year. Synthetic routes to glycerol were redundant and only a single manufacturer of high purity glycerol remains in business. Various options are being investigated. A route has been patented to convert glycerol to methanol – not a valuable chemical but a more economical outlet than combustion.⁶ The glycerol is passed over a supported precious metal catalyst at temperatures of about 100°C in the presence of 20 bar of hydrogen. The carbon–carbon bonds of glycerol are broken but the carbon–oxygen bonds remain intact, thus avoiding the production of methane and carbon dioxide.

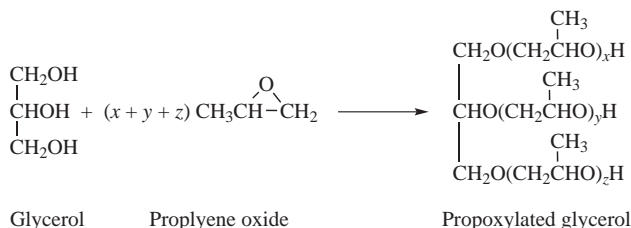


Meanwhile, METabolic Explorer has announced plans to build a 50,000 metric ton/year plant to produce 1,3-propanediol biotechnologically, and Glycos Biotechnologies has announced plans to make 20,000–30,000 metric tons/year of isoprene, ethanol, and acetone.⁷ Both these initiatives are to be undertaken in Malaysia where the glycerol will presumably be generated by Malaysian production of biodiesel from palm oil.

15.11.1 Established Glycerol Uses

Dynamite is glyceryl trinitrate (nitroglycerin) adsorbed on wood pulp. The compound is also used as a coronary vasodilator for angina pectoris. It is delivered either as a sublingual tablet or a transdermal patch. Although it has been used for at least a century, its mode of action via the blood's nitric oxide pathways has only recently been discovered. Glycerol competes with other polyols such as ethylene glycol, pentaerythritol, and sorbitol as a raw material for alkyd resins (Section 11.1.2) and also for polyethers for polyurethanes (Section 9.3.1).

Glycerol's most important chemical use is in alkyd resins (Section 11.1.2) and to a lesser extent in unsaturated polyester resins. Alkyds are condensates of glycerol or pentaerythritol (Section 5.11.3) with phthalic anhydride and fatty acids. They are the major vehicles for oil-based paints, but their use has declined because of the trend towards nonsolvent-based coatings. When reacted with propylene oxide, glycerol yields a coreactant that gives polyurethane resins (Section 9.3.1) with isocyanates. Trimethylolpropane is usually preferred to glycerol in this application.



Glycerol monoesters, for example, the monooleate and the monostearate, are used as nonionic surfactants especially in the food industry. Triacetin (glyceryl triacetate) is an antifungal used against athlete's foot, a fixative in perfumery, and a plasticizer for the cellulose acetate filter tips in cigarettes.

15.12 ALCOHOLYSIS OF FATS AND OILS

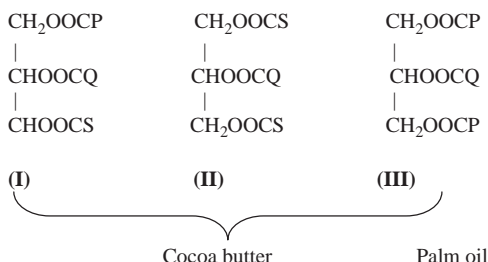
One of the most important commercial reactions of fats and oils is ester interchange or alcoholysis. Biodiesel is currently a rapidly growing market (see below). Mono- and diglycerides for food emulsifiers are made this way – by Eastman, for example. If a triglyceride is heated with a polyol such as glycerol or pentaerythritol in the presence of a suitable catalyst such as sodium methoxide, mixed partial esters are obtained. The partial esters may then be reacted with a dibasic acid or its precursor to give an oil modified alkyd resin.⁸ If the partial esters are reacted with toluene diisocyanate, oil modified urethanes are obtained. The mixture of mono- and diglycerides is also widely used in food emulsifiers.

15.12.1 Cocoa Butter and Mothers' Milk

Transesterification of triglycerides has a significant application in the production of synthetic cocoa butter, infant feeding formulas, and *trans*-fat-free triglycerides. As a general rule, triglycerides from animal sources (fats) are solid at room temperature, while fish and vegetable oil triglycerides are liquid. Cocoa butter is unique in being the only solid vegetable triglyceride. It is pressed from cocoa beans that have been harvested and fermented so that the pulp can be drained.

Cocoa butter consists of triglycerides that are mixed esters of palmitic acid ($\text{C}_{15}\text{H}_{31}\text{COOH}$), oleic acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$), and stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$). Only the oleic acid contains a double bond. If the alkyl residues are represented as P, Q, and

S, respectively, then the main triglycerides in cocoa butter are **(I)** and **(II)** and **(III)** below.



Nature, in her wisdom, has not provided the correct ratio of cocoa to cocoa butter in the cocoa bean, for there is not enough butter to turn all the cocoa solids into chocolate. Some cocoa solids may be sold on their own as the base for beverages, but there is still a surplus.

The use of cocoa butter replacements is tightly regulated in many countries. In some instances, including the EU, a minor addition of 5% is permitted to help increase stability of the chocolate. This involves increasing the natural SOS (stearic–oleic–stearic) arrangement of residues in cocoa butter through addition of SOS rich substitutes. The product still falls under the Chocolate Standard of Identity.

Meanwhile, chocolate must contain a minimum of 35% cocoa components. If a product contains less than that, it is called cocoa fantasy. It may be blended with alternative fats to give a low grade chocolate, which may be designated as a “chocolate flavored coating.” Thus the central problem of the chocolate industry is to get value out of the surplus cocoa and to find effective cocoa butter substitutes, of which several have been developed.

The first group is called CBEs (cocoa butter extenders) and must have a triglyceride composition similar to cocoa butter to work satisfactorily. Thus PQS, PQP, and SQS need to be the main triglycerides with very little PSQ, SSQ, or PPQ (see beginning of this section for nomenclature) and no short chain fatty acids. The second group is called CBSs (cocoa butter substitutes), and they can have compositions that deviate from cocoa butter, but have a similar melting profile. Palm oil **(III)** is sometimes used, as are palm kernel oil and coconut oil, which contain about 50% lauric (dodecanoic) acid, mainly as trilaurin.

CBSs have two limitations. They lack the volatile flavor constituents of cocoa butter, and they rarely have the exact melting and crystallization characteristics. Cocoa butter melts over a range and becomes completely liquid just below the temperature of the mouth, hence a high quality chocolate will “melt in the mouth” in a satisfying way.

The potential market for cocoa butter replacements is huge. World production of cocoa beans is about 3.5 million metric tons/year, almost half of it (43% in 2009) coming traditionally from the Ivory Coast. This pattern has recently been disturbed by a political crisis in which the reigning head of state refuses to step down in spite of losing an election. The supplies of chocolate have been reduced and the price has

risen. Most of the remaining cocoa beans come from Ghana, so that 80% of world supplies come from West Africa. They are harvested mainly by child labor under conditions varying from merely unpleasant to actual slavery.

World production of cocoa butter is about 1.5 million metric tons, compared with about 16 million metric tons of soybean oil and 6 million metric tons of butter. North Europeans eat the most chocolate (Ireland 11.2 kg/year/person in 2005; Switzerland 10.7; Britain 9.8; Germany 8.3). South Europeans eat less (Italy 2.5; Spain 1.7) because their climates are hotter, and chocolate melts. The United States occupies an intermediate position with 5.4 kg/year/person. The range of climatic conditions that favor cocoa beans is very narrow, and among the gloomier predictions of the consequences of global warming is that it would make cocoa beans impossible to grow.

Cocoa butter is expensive but palm oil, which resembles it in structure, is cheap and readily available. Basically, some of the palmitic residues in palm oil need to be replaced by stearic residues. Unilever devised a process in the 1970s in which a mixture of palm oil and stearic acid was treated with a 1,3-specific lipase (*Mucor miehei*) immobilized on kieselguhr. The solvent was *n*-hexane saturated with water. The tiny amount of water that dissolves in hexane meant that appreciable overall hydrolysis did not take place. Instead, processes of hydrolysis and reesterification took place at 313°C over a few hours.^{9,10}

This process was replaced by an enzymatic process, later used for *trans*-fat-free fats (see below) and devised originally for infant feeding formulas. Unilever sold its industrial specialty fats division to IOI Loders a few years ago, and the cocoa butter extender is marketed by them, along with the infant feeding formula manufactured by a similar process.¹¹

15.12.1.1 Mothers' Milk

Typically the vegetable fats that are used in traditional infant formulas contain less than 20% of the saturated fatty acids in the 2 position (i.e., the central position on the glycerol chain). Palmitic acid is the most abundant, making up 20–25% of the total fatty acid content, but mainly in the 1 and 3 positions (i.e., the end positions). Mothers' milk, on the other hand, has an unusually large proportion – about 60–70% – of palmitic acid attached to the central position. The 1 and 3 positions are occupied by oleic or linoleic residues. This apparently minor difference has a major impact on the infant's ability to digest, absorb, and metabolize nutrients. In particular, palmitic acid residues in the 1 and 3 positions (as in vegetable oils) are excreted as calcium salts, depriving the infant of both nutrients and increasing the hardness of stool. The enzymatic process rearranges these residues to give a product Betapol™, in which about 55% of palmitic residues are in the 2 position.¹²

15.12.2 Trans Fats and Interesterification

The danger of *trans* fats, produced when oils are hydrogenated, was mentioned in Chapter 13 and they now rank above the long-established saturated fats as a danger to

cardiac health. A novel method of producing fats without *trans* groups was developed by Archer Daniels Midland (ADM), based on interesterification. Initially, a quantity of vegetable oil is completely hydrogenated, so that all the side chains are saturated. This is then interesterified with more vegetable oil in the presence of an immobilized enzyme that ADM had developed (Novozyme, Lipozyme®). Because the oil has not been hydrogenated, it contains no *trans* linkages. The saturated side chains of the first vegetable oil transesterify with the unsaturated side chains of the second oil to give the desired degree of hardness, without *trans* linkages. Furthermore, by choice of a vegetable oil that hydrogenates to give stearic acid side chains, which are generally agreed to have little effect on blood cholesterol, a truly healthy fat should be formed.

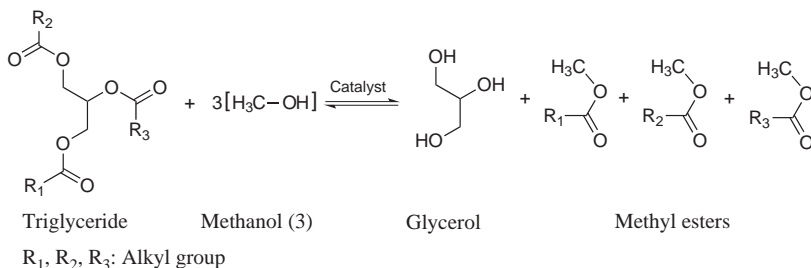
Unilever has been producing *trans*-free solid fats from fully hydrogenated oil esterified with liquid vegetable oils since 1994, but theirs was a less sophisticated process.

Commercialized in 2002, 15 million pounds (6800 metric tons) of interesterified fats had been produced by 2005. Alas, in 2007, the possibility arose that interesterified fats, for reasons not understood, were as bad for the cardiovascular system as *trans* fats. This was based on a single limited study,¹³ and the diets differed in overall fatty acid composition – the interesterified fat had 30% more saturated and 57% less monounsaturated fatty acids than the untreated palm olein. Further work on fat metabolism is in progress¹⁴; meanwhile, almost any fat product labeled as free of *trans* fats is likely to contain interesterified fats.

15.12.3 Biodiesel and Lubricants

Concern about biodegradability, pollution, and depletion of nonrenewable resources has led to the development of fuels and lubricants based on fats and oils.¹⁵ Thus in the early 1990s “biodiesel” fuels emerged. These consist of the methyl esters of animal or vegetable oils such as rapeseed, sunflower, or tallow compounded with additives similar to those used for petroleum-based diesel fuel. They are known collectively as FAMES (fatty acid methyl esters). Ethyl, propyl, and higher esters could in principle be used, but they are less volatile and more expensive.

Palm oil is most commonly used. It is treated in a batch process with methanol in the presence of sodium hydroxide in ethanol. A slight excess of alkali is added to neutralize free fatty acids present in the vegetable oil. The reactants must be carefully dried, otherwise straightforward saponification occurs to give soaps. Typically a temperature of about 70°C is used and reaction times vary between 1 and 8 hours.



The by-product glycerol separates out as a dense lower layer. Excess alcohol is removed by flash evaporation or distillation.

Other production processes include supercritical methanol and high temperatures, which mean that a catalyst is unnecessary. Some methods use microwaves and ultrasound. There is a lipase catalyzed method, which used methyl acetate for the transesterification because methanol poisoned the lipase.

Waste vegetable oil (WVO) from the catering industry is also used as a feedstock. It has to be filtered to remove dirt, charred food, and other nonoil material. Water too must be removed, because its presence causes hydrolysis of soaps. A top Beverley Hills cosmetic surgeon (only in California!) said in 2008 that he used fat he removed from patients in liposuction operations to power his “green” 4 × 4 car. It turned out that there is a law against using human medical waste to power vehicles. His clinic had to close. It is difficult to understand why, in that he was simultaneously attacking the twin problems of obesity and the energy crisis.

The biodiesel, based on the methyl esters of fatty acids, unlike its petroleum-based counterpart, is free from sulfur. On combustion it is said to produce less smoke, less hydrocarbons, and less carbon monoxide. Emission of nitrogen oxides formed at the high combustion temperatures, however, is not reduced.

Diesel fuels are labeled according to the amount of biodiesel they contain. One containing 20% biodiesel is labeled B20. Pure biodiesel is B100. B20 can be used directly in diesel engines but B100 requires some engine modification.

The interest in biodiesel fuels has also increased, because they burn more cleanly. Although they are attractive, there are two problems. The first is how to dispose of coproduct glycerol. The second problem is one of supply. In 2009, the world produced 128 million metric tons of fats and oils, of which 88% was used for human food. Correspondingly, the United States alone used 44,247 million gallons of gasoline equivalent of diesel fuel in 2006, which is approximately 133 million metric tons. Of this, biodiesel formed 0.58%, a tiny proportion.

Viewed another way, global palm oil production has soared from 300,000 metric tons in 1995 to 41 million metric tons in 2009. The European Commission’s Renewable Transport Fuels Obligation required 3.25% of all fuel sold in 2010 to come from crops and requires it to be 13% by 2020. The area of land required to meet this target is about as large as Spain, France, the British Isles, and Germany put together.¹⁶ It is claimed that biofuels should reduce emissions by 35% compared with fossil fuels, but this implies sustainably sourced oil and neglects the carbon released when forest and grassland is turned into plantations.¹⁷ Calculations taking this into account predict an increase of 31%,¹⁸ and they suggest that it takes 840 years for the carbon dioxide released when rain forest is burned to be absorbed. The expansion of the palm oil industry in Indonesia has made it into the world’s third largest CO₂ emitter after the United States and China. The orangutan is on the brink of extinction in Sumatra, because of rain forest destruction. And all this is being paid for by a lavish subsidy to biofuels from European taxpayers.

It is therefore doubtful if oil and fat production should be increased to the point that would allow it to gain more than a niche market as a diesel fuel replacement. However, in areas in the world with a high ecological sensitivity, dimer acid esters

(Section 15.5) have been used as fuel in two-cycle engines. Introduced in the early 1990s were oils for two-cycle engines based simply on esters of dimer acids. These were intended as fuels for engines for lawnmowers and outboard motor boats and for engines for motor cycles, to replace the normal smog-producing motor oil–gasoline mixture. The problem with the motor oil–gasoline is well demonstrated in Bangkok, where two-cycle engines on motorcycles and small taxis produce a serious smog problem. This is an example of a niche market for fatty-based fuels. They compete with a combination of gasoline with polybutenes (Section 7.2.3) and mixtures of propane and butane (LPG; Fig. 4.3). The latter are actually in use in Bangkok today, an infrastructure having been developed for liquid petroleum gas (LPG) distribution.

Of potential importance is the use of biodegradable fatty materials as lubricants. The lubricity of fatty materials is well established, and our ancestors used tallow on the moving parts of their chariots in 1400 B.C. Esters with lubricant properties have been known since World War II, and synthetic lubricants for automobiles today may contain pentaerythritol tetraesters (Section 5.11.3) and esters of dibasic acids such as the di-(2-ethylhexyl) ester of azelaic acid (Section 15.7). Such compounds become much more biodegradable in the form of their fatty acid counterparts, and such materials are being proposed for use in automobiles, and as metal working lubricants, turbine oils, hydraulic fluids, and functional fluids generally.

15.12.3.1 *Algae*

Algae are efficient oil producers and can produce cells containing more than 70% oil by mass. They do not compete for agricultural land, nor call for the destruction of rain forest, and their oils – triglycerides – contain the same amount of energy as oils such as palm oil, which can be used as diesel fuel. Algae will grow in ponds or rivers and, indeed, they have been a problem in the past because discharge of nutrients into river has led to eutrophication and the “death” of waterways. They have nonetheless been evaluated as a source of oils, but with limited success. Growing algae in waterways – the photosynthetic method – results in a very expensive product.

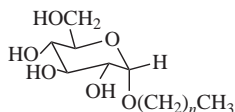
It turns out that the photosynthetic method involves two stages: first, light converts the carbon from carbon dioxide to sugars inside the cell, then the sugars are converted to oil. The first process is very inefficient: a dense pond of algae is less efficient than sugar cane in fixing carbon dioxide. Much of the light is dissipated as heat; little reaches the algae below the surface. The second process is rapid.

A U.S. company, Solazyme, has pioneered a so-called heterotrophic fermentation of algae.¹⁹ They are fed in the dark with carbohydrates such as sugar cane or cellulosic biomass. The algal fermentation is much cheaper than photosynthesis, as the algae grow much faster and yield more biomass per liter with a higher percentage of oil per cell. In 2010 Solazyme provided over 50,000 gallons of oil to the U.S. Navy for evaluation.

Solazyme claims that genetic engineering allows them to modify the metabolic pathways so that they can match commercial oils. Even as fuel, they can offer a purer product containing less sulfur and phosphorus than diesel.

15.13 ALKYL POLYGLYCOSIDES

A family of nonionic surfactants for detergents, commercialized by both Henkel and Air Liquide in the early 1990s, is called alkyl polyglycosides and is the first important fatty acid derivatives with an acetal linkage. They comprise acetals of a mixture of mono- and disaccharides of glucose, from which an acetal or glucoside has been formed with a fatty alcohol with 10 to 14 carbon atoms. The formula for a product from glucose and an alcohol where $n = 9\text{--}13$ is



The use of the term glycoside indicates that sugars other than glucose may be involved. The preferred process for manufacture appears to involve two steps. In the first, the sugar reacts with *n*-butanol in the presence of weak acid to form an acetal. In the second, this intermediate reacts with a $C_{10}\text{--}C_{14}$ fatty alcohol mixture to give the glucoside surfactant, with the release of the *n*-butanol for recycle.

The products are biodegradable and are said to be “green” since the sugar portion comes from corn starch and the fatty alcohols from coconut or palm kernel oil. The products are being targeted for shampoos and specialties such as cosmetics, as well as for laundry and dishwashing detergents.

These products are related to the sugar esters – C_{12} to C_{18} partial fatty acid esters of sucrose – which have been popular in Japan as nonionic rapidly biodegradable surfactants for many years. In 1995 Proctor & Gamble announced that it was replacing a portion of the alkylbenzene sulfonate in heavy duty detergents with a sugar-based surfactant.

15.14 NONCALORIC FAT-LIKE SUBSTANCES

Although fat chemistry appears to be mature, there are growing problems of cardiac health, obesity, and excessive fat intake. There is a huge market for nonnutritive substances that function like fats for those who feel themselves to be overweight. Proctor & Gamble developed a fully esterified fatty acid ester of sucrose called “Olestra.” It was said to have the mouth feel, taste, and cooking and baking functionality of triglyceride fats. The product was made by an ester interchange reaction between sucrose, dissolved in water and soap, with fatty acid methyl esters. Apparently esters from several oils are useful, but the patents stress the highly unsaturated safflower oil. Other reports say that in practice the cheap saturated stearic acid was used. A typical structure is shown in Figure 15.7, with one hydroxyl left unesterified to show the functionalization site.

The methyl esters were prepared by an alcoholysis reaction between safflower oil and methanol. The coproduct was glycerol and, had the product been a success, it

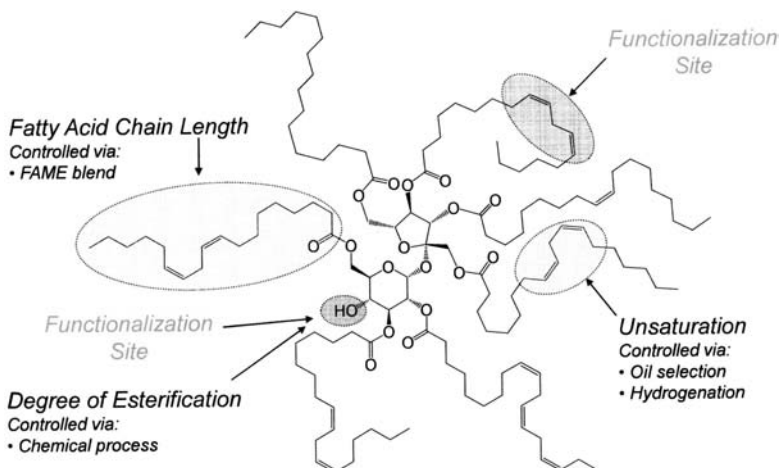


FIGURE 15.7 Structure of “Olestra.” (Source: Proctor & Gamble, acs.confex.com/acs/green09/recordingredirect.cgi/id/537.)

might have led to a 50% world oversupply of glycerol. The problem, however, did not arise. Olestra was commercialized initially in a brand of potato chips. It turned out to deplete oil-soluble vitamins, which had to be replaced in diet. Its lubricating properties, and the fact that it was not broken down in the digestive system, meant that, in some consumers, it led to anal leakage. The consumer response was poor and Proctor & Gamble sold the food application. Nevertheless, Olestra is still available in low calorie potato chips.

There is, however, a happy ending. Sucrose esters turned out to have another application and are marketed under the name Sefose® for use as industrial lubricants and paint additives.²⁰ They are tailored to work synergistically with alkyd resins (Section 11.1.2). They start as part of the solvent system but the double bonds in the side chains crosslink with double bonds in the alkyd so they eventually become part of the paint film. They are not volatile and enable a reduction in the amount of other solvent used with them. They are not toxic and are fully biodegradable and certainly “green.” Their market penetration remains to be determined but there is a huge market. In 2006, 1.2 million metric tons of solvents was used in the U.S. coatings sectors, of which 45% were hydrocarbons, aromatics (e.g., xylene, toluene), and aliphatics (e.g., hexane, decane).

ENDNOTES

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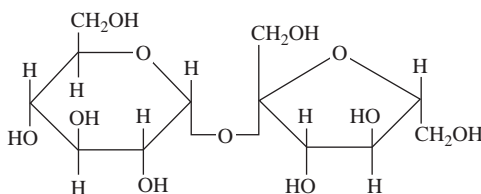
CHAPTER 16

Carbohydrates

Carbohydrate sources for chemicals may be subdivided into four main groups: sugars, starch, cellulose, and the so-called carbohydrate gums. In addition, there are miscellaneous sources such as the pentosans found in agricultural wastes, from which furfural is made. We consider each of these as a source of chemicals. Fermentation processes are mainly carried out on carbohydrate substrates, so they too have been included in this chapter, together with scenarios based on the possibility of petrochemical feedstocks becoming depleted or renewable sources becoming necessary.

16.1 SUGARS AND SORBITOL

For the chemist, the term sugar covers a multitude of mono-, di-, and trisaccharides, composed of pentose and hexose units. In ordinary speech, however, it generally means sucrose. Sucrose is a major constituent of diet; the average citizen of a developed country consumes about 40 kg – about two-thirds of his/her body weight – annually. It is the purest crystalline organic substance to be sold in quantity to the general public, routinely reaching 99.96% purity on an anhydrous basis.



Sucrose

Sucrose is extracted from sugar cane, which is a member of the grass family, or sugar beet, which is a root crop. The cane is chopped and crushed and juice extracted, sometimes with the aid of water or weak juice. The residue, bagasse, is a

fairly pure cellulose. It was formerly burned as fuel to make the sugar refinery self-sufficient for energy or else it was converted to paper or hardboard. It may also be burned to generate electricity, and technical improvements have led to electricity from bagasse being fed into the Brazilian national grid. One metric ton of bagasse at 51% solids is equivalent to a barrel of oil.

The juice is purified and clarified and concentrated from about 85% water to 40% water in triple or quadruple effect evaporators, to conserve energy by reuse of heat. Vacuum evaporation supersaturates the liquid, and seeding precipitates sugar crystals, leaving blackstrap molasses. This is used as cattle feed, as a substrate for fermentation to produce citric acid, for rum making, and for other fermentations. In chemical terms, the extraction of sugar from sugar beet is similar, although both processes are far more complicated than is indicated above.

World production and consumption of sugar are indicated in Figure 16.1. Western Europe, India, and Brazil are the largest producers and consumers, the first growing sugar beet and the other two sugar cane. Brazil, Western Europe, Australia, and Thailand are the major exporters, and the Russian Federation, Western Europe, China, Indonesia, and the United States are the major importers. Cuba was at one time a significant producer but has declined because of the political problems of enmity to the United States and the economic problems of a command economy.

Obesity and high sugar consumption correlate with diabetes, and 11% of U.S. citizens suffer from this disease. Chinese per capita sugar consumption has risen by 48% since 2001 and, while, per capita consumption is only 29% of that of Americans,

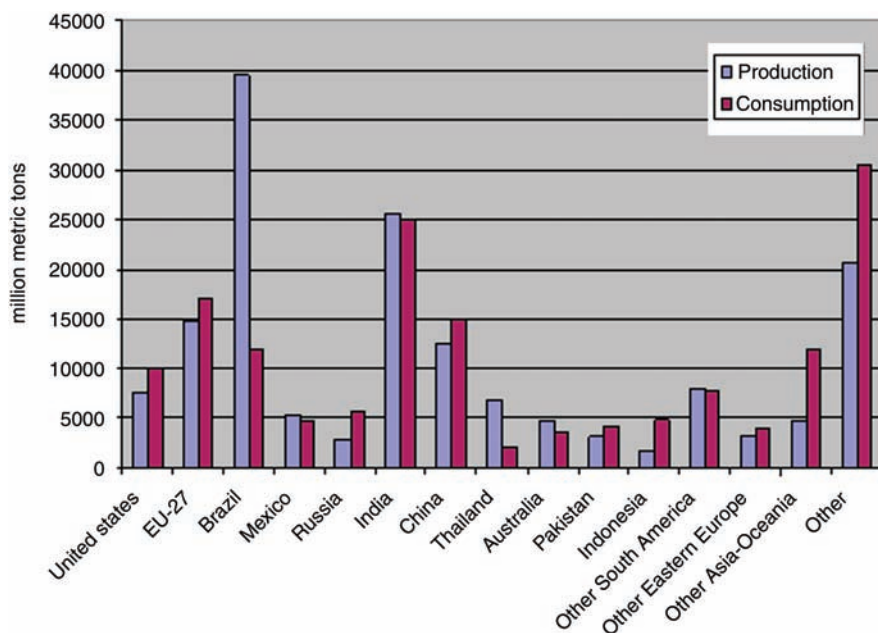


FIGURE 16.1 World sugar production and consumption 2009/2010.

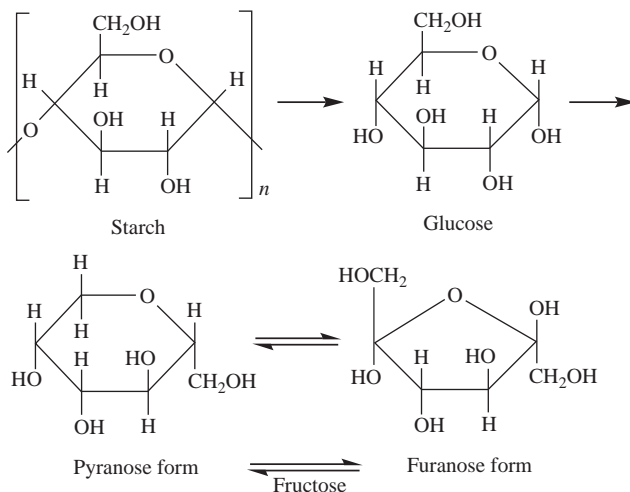
the diabetes rate has soared to 10% – an incredible 92.4 million cases. Chinese plans to double their output of high fructose corn syrup by 2013, to become the world's largest producers, suggest that the problem will get worse.¹

There are few chemical uses for sucrose. Sucrose octaacetate is used as a denaturant in ethanol. The acetate, isobutyrate, and octabenzoate are used as plasticizers. The mono- and difatty acid esters are surfactants, sucrose polyether polyols may be used in polyurethane formulations, and sucrose fatty acid esters are used in alkyd resins and low-fat potato chips (Section 15.14).

The bacteria *Leuconostoc mesenteroides* and *Lactobacteriaceae dextranicum* convert sucrose to dextran, a polysaccharide consisting of a backbone of D-glucose units linked predominantly α -D(1 \rightarrow 6). This is used as a plasma volume expander for transfusion for problems such as burns, where there is a drastic loss of body fluids. Dextran competes with “natural” materials such as fresh frozen blood plasma and albumen, and with degraded gelatin and hydroxyethyl starch. In the past, the “natural” products have been preferred where available, but with the current anxiety about infected blood, dextran has benefited.

D-Glucose, known as dextrose (a contraction of dextrorotatory glucose), is manufactured on a large scale from corn starch, which is hydrolyzed by a mixture of acid and the enzyme glucoamylase, producing a syrup of high nutritive value but not as sweet tasting as sucrose. Sweeteners obtained in this way are in principle cheaper than sucrose.

D-Fructose is isomeric with D-glucose but is sweeter and therefore offers the opportunity for a reduced calorie diet without sacrificing “sweetness.” It is produced by the action of three enzymes on starch. The first is an immobilized amylase that degrades the starch to lower molecular weight polymers; the second is an immobilized amyloglucosidase that converts these oligomers to glucose; and the third is an isomerase that changes the glucose to fructose. The isomerase may be adsorbed on an insoluble carrier or fixed within the cellular microorganism in which it occurs. This technology was made possible by the development of enzyme immobilization.



Crystalline D-fructose is more hygroscopic than dextrose and requires special packaging. Hence it is usually used as a syrup (high fructose corn syrup; HFCS) in soft drinks, confectionery, and foodstuffs.

Sweeteners based on corn make up about 40% of the U.S. sweetener market.² High fructose corn syrup production started in 1967 and, as illustrated in Figure 16.2, by 2003 it had equaled the consumption of refined sugar (sucrose). Reasons for this include governmental production quotas of domestic sugar, subsidies of U.S. corn, and an import tariff on foreign sugar. All of these combine to raise the price of sucrose to levels above those of the rest of the world, making HFCS cost-effective for many sweetener applications. The average American consumed approximately 37.8 lb (17.1 kg) of HFCS in 2008, versus 46.7 lb (21.2 kg) of sucrose. There was then a reaction against it partly on the grounds that it was unhealthy, although the evidence was thin, and partly that sucrose tasted better. There was also publicity given to the obesity problem. In 2010, The Corn Refiners Association applied for permission to use the name “corn sugar” in place of high fructose corn syrup. Meanwhile, consumption has declined.

In Western Europe, pressure from the sugar farmers has led to the imposition of a quota within the European Community. In 2005, this was set at 303,000 metric tons, which is tiny compared with overall EU consumption of about 17 million metric tons.

Figure 16.2 does not show honey – only sold in small amounts – or lactose. Lactose occurs to the extent of about 5% w/v in milk and is extracted from waste skim milk. It is used as an acidulant in foods, in cheese production, in printing and dyeing, and in

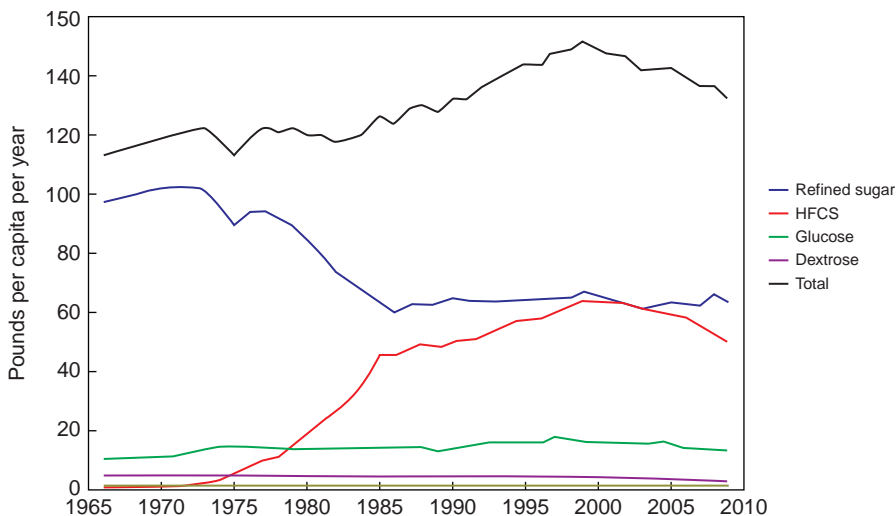
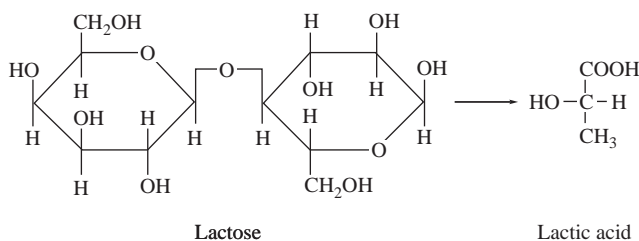


FIGURE 16.2 The U.S. consumption of various sweeteners 1965–2009. HFCS = high fructose corn syrup. (<http://www.ers.usda.gov/Briefing/Sugar/Data.htm> via Wikipedia.)

leather production. Fermentation of whey, lactose, sucrose, or glucose with *Bacillus acid lacti* or related *Lactobacilli* gives lactic acid:



Lactic acid is the monomer for a polymer, poly(lactic acid) or polylactate, which provides a biodegradable plastic (Section 19.12).

Glucose may be oxidized to gluconic acid, reduced to sorbitol, and converted to a lactone, α -methylglucoside, as shown in Figure 16.3. Gluconic acid is primarily used as a food additive, and α -methylglucoside has been of some interest in alkyd resins. Surfactants based on glucose and fatty alcohols are described in Section 15.14.

Sorbitol is the starting material for the classic synthesis of vitamin C (ascorbic acid) shown in Figure 16.4. The crucial stage is the second, and it is an early example of the use of biotechnology to supplement the synthetic skills of the chemist. Conversion of D-sorbitol to L-sorbose would present a formidable problem in organic chemistry.

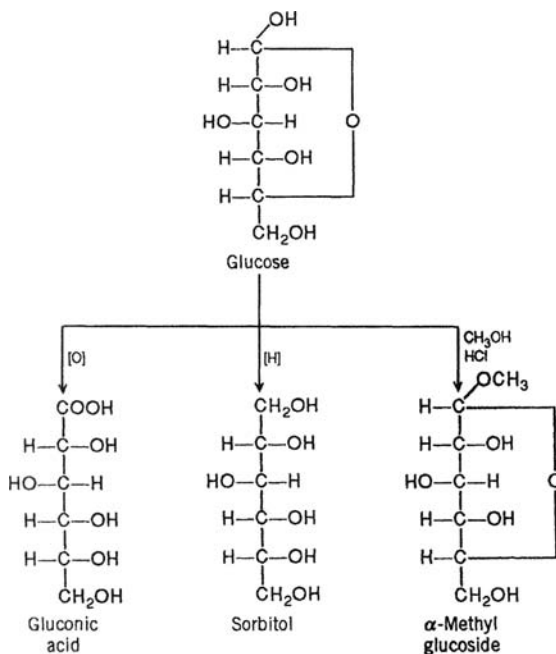


FIGURE 16.3 Reactions of glucose.

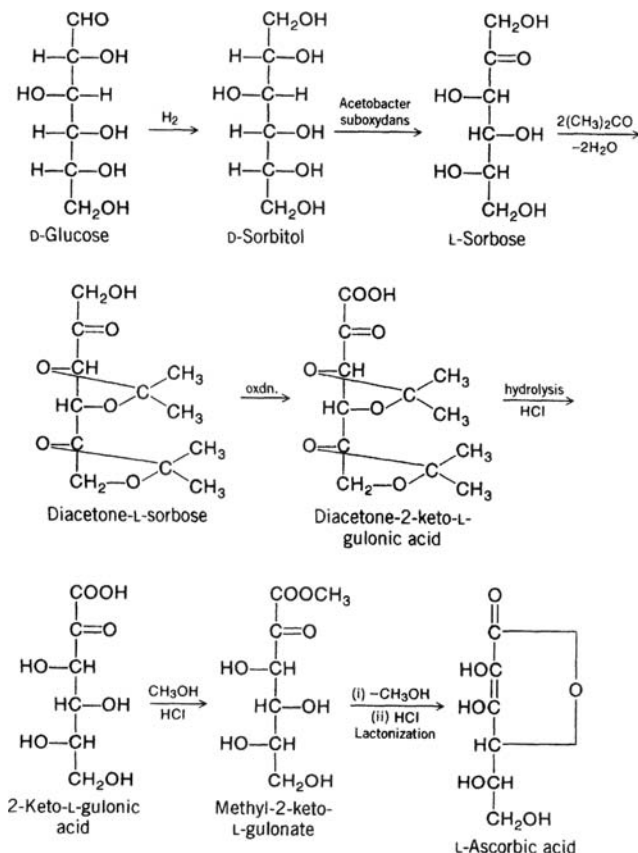
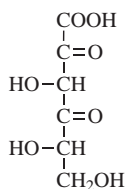


FIGURE 16.4 Synthesis of vitamin C (ascorbic acid).

The appropriate bacterium, *Acetobacter suboxydans*, selectively oxidizes the hydroxyl group on the C2 of sorbitol, making feasible the remainder of the synthesis.

A biotechnological synthesis of ascorbic acid was announced in 1988 by Genencor International and Eastman Chemical. Glucose is converted to 2-keto-L-gulonic acid (see Fig. 16.4) in two steps as compared to five steps in the traditional process. In the first step, an organism such as *Erwinia herbicola* converts glucose to 2,4-diketo-L-gulonic acid:



In the second step, the diketo compound is converted to 2-keto-L-gulonic acid using a *Corynebacterium*.

Sorbitol is also the source of a range of surfactants – the sorbitan esters and ethoxylated sorbitan esters (Fig. 16.5). These have been marketed for about 40 years. Sorbitol is simultaneously dehydrated and esterified with stearic, palmitic, lauric, or oleic acid, to give mono- or tri-substituted sorbitan esters. A mixture of esters is obtained in both cases, and the hydroxyls are esterified more or less randomly. The sorbitol can also lose another molecule of water to give isosorbide (Fig. 16.5 upper right), which remains in the reaction mixture and is also esterified. Sorbitan esters are often water insoluble but are used as solubilizers in the oil phase and are also approved

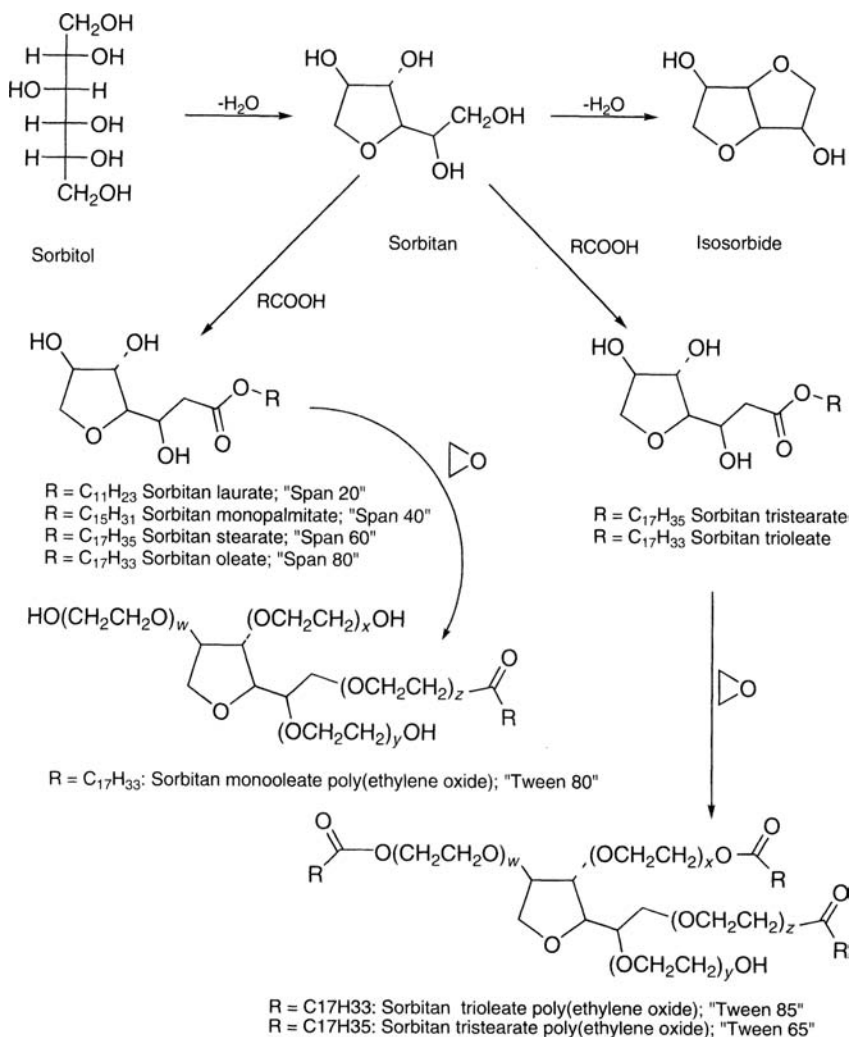


FIGURE 16.5 Sorbitan esters and ethoxylated derivatives ($w + x + y + z = 20$).

for human consumption. Hence they are used as emulsifiers in drinks, cosmetics, pharmaceuticals, and foods. The most widely known trade name is "Spans," and a range of compounds are available depending on the esterifying groups.³

Treatment of the sorbitan esters with ethylene oxide leads to an ethoxylation/transesterification process in which all four of the hydroxyls originally present in the sorbitan are ethoxylated and one or three fatty acid groups migrate to esterify some of the terminal hydroxyls. Again, the positions of the fatty acid residues are more or less random, and the positions shown in the figure are only illustrative. The ethoxylated derivatives are water soluble and are known as polysorbates or by the trade name "Tweens." They are used as industrial emulsifiers, antistatic agents, fiber lubricants, and solubilizers. For example, Tween 60, an ethoxylated monostearate, is used to stabilize "synthetic" whipped cream, the stearate having less flavor than the oleate.

Sorbitol is also used as a diluent in nonnutritive sweeteners, for example, mixed with aspartame to provide bulk, so that consumers can sprinkle teaspoonfuls of sweetener on their breakfast cereal instead of having to measure out a tiny quantity of pure aspartame.

16.1.1 Isosorbide

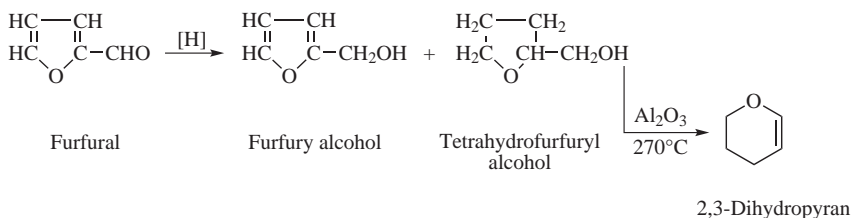
As indicated above, the removal of 2 moles of water from sorbitol yields isosorbide, a bicyclic compound with two hydroxyl groups. It was early discovered that the mono- and dinitrates of isosorbide are useful for the treatment of heart diseases, primarily angina pectoris. It has also been proposed for use in unsaturated polyesters (Section 11.1.3) for the glycol component. Its long chain esters are useful as plasticizers (see Section 11.1.1). Of current interest is its bis-epoxypropyl ester as a replacement for bisphenol A (BPA) in epoxy resins (Section 9.1.2.1). BPA has been believed to exhibit human toxicity (Section 9.1.2.4). The proposed bis epoxy compound could replace bisphenol A in epoxy and polycarbonate resins, which are used, for example, in toys and baby bottles. Naturally, the danger of bisphenol A and the efficacy of the new material must be proved before replacement is warranted.

16.2 FURFURAL

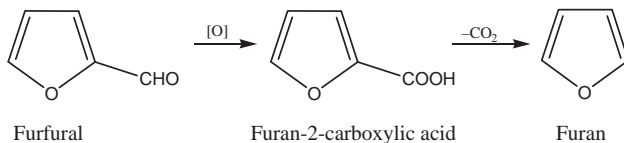
Oat hulls, corn cobs, sugar cane stalks, wood, and many other vegetable wastes contain polymers (pentosans) of pentose sugars such as arabinose. On dehydration with hydrochloric or sulfuric acid, furfural is produced. Furfural is used as a selective solvent in petroleum refining and has been used in the extractive distillation of butadiene to separate it from other C₄ olefins (Section 7.1). With phenol it gives phenol-furfuraldehyde resins, which are used to impregnate abrasive wheel and brake linings.

Reduction of furfural gives furfuryl alcohol and tetrahydrofurfuryl alcohol, and the latter can be dehydrated and its ring expanded by passage over an alumina catalyst at 270°C. The product is 2,3-dihydropyran. The largest use for furfural in the United States is for conversion to furfuryl alcohol, which in turn undergoes an acid-catalyzed

condensation polymerization to yield resins useful as binders in the preparation of foundry cores for molding.

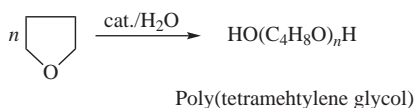


Catalytic decarbonylation or oxidation followed by decarboxylation gives furan.



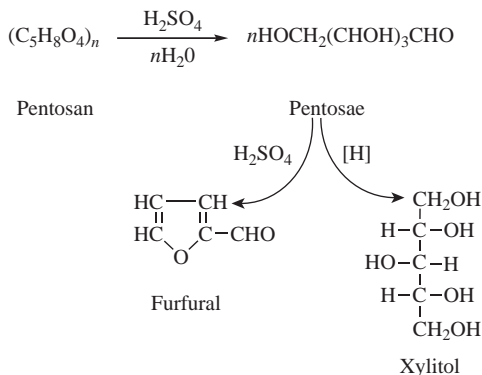
Tetrahydrofuran is made by the decarbonylation of furfural with a zinc–chromium–molybdenum catalyst followed by hydrogenation. It is also made by the dehydration of 1,4-butanediol (Section 12.3.1) and by the hydrogenation and hydrogenolysis of maleic anhydride or maleic esters. These are by far the largest sources, the furfural route accounting for less than 10% of U.S. production.

Like ethylene and propylene oxides, tetrahydrofuran can be oligomerized to a polyether with hydroxyl end groups. The polymer is called poly(tetramethylene glycol) and is a component of the elastomeric fiber Spandex (Section 7.1.6.8).

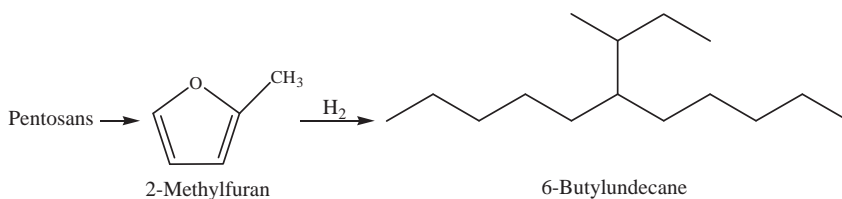


Until 2001 there was a single major producer of furfural in the United States, Penn Specialties, which acquired the technology from Great Lakes Chemical, which in turn acquired it from the Quaker Oats Company, which pioneered it. About six tons of corn cobs or other vegetable wastes are required for every ton of liquid product, so collection of feedstock involves high labor costs, and Penn has since gone bankrupt.

Another development that bears on furfural is the interest in the sugar alcohol, xylitol, as an ingredient in chewing gum, candy, and sweet cereals. The idea is to prevent dental caries. Xylitol, like furfural, is derived from pentosans. The pentosan xylose, derived from hardwood or maize, is hydrogenated to xylitol by conversion of the aldehyde group to a primary alcohol. The largest manufacturer globally is the Danish company Danisco, with several other suppliers from China.

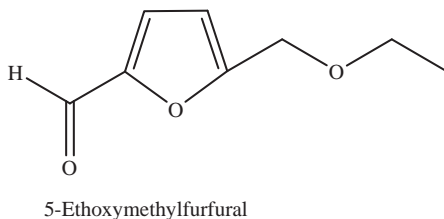


A process has been demonstrated on a laboratory scale by which three molecules of 2-methylfuran can be converted into high quality diesel fuel by hydroxyalkylation/alkylation and hydroxydeoxygenation⁴:



The hydroxyalkylation/alkylation stage can be performed on a variety of aldehydes, notably 5-hydroxymethylfurfural and 5-methylfurfural, obtained by hexose dehydration. The benefit of this route to diesel, if it can be scaled up, is that it uses agricultural wastes rather than food-grade oils.

A Dutch firm, Avantium, is commercializing a route from cellulose to 5-ethoxymethyl furfural, potentially usable in diesel fuel.¹³



16.3 STARCH

Starch is one of the most important chemical products of the vegetable kingdom and is found in practically all plant tissues, especially in seeds (e.g., wheat and rice) and

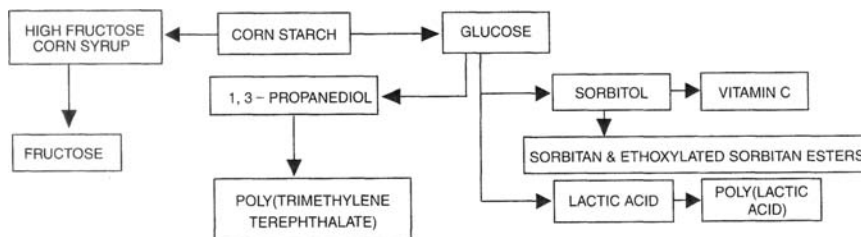


FIGURE 16.6 The corn starch value chain.

tubers (e.g., potatoes). Commercial starch in the United States is extracted chiefly from corn and to a lesser degree from wheat. In Europe, potatoes are an important source.⁵

The use of corn as a source of starch is only one of an extensive range of uses. Corn is primarily used in foodstuffs. Its protein, known as gluten, occurs in various food formulations. Corn oil is one of the most important cooking oils. Meanwhile, starch itself has a value chain shown in Figure 16.6. About half the starch produced in the United States is hydrolyzed with hydrochloric acid to glucose or partially hydrolyzed to starch-glucose syrups that can be sold as such or isomerized to fructose (Section 16.2). Its conversion to sorbitol, sorbitol derivatives, and vitamin C has already been described. Starch-derived glucose is a substrate for fermentation processes giving lactic acid [hence poly(lactic acid), Section 19.12]] and 1,3-propanediol (Section 5.11.6.6), which is a component of poly(trimethylene terephthalate).

Chemically, starch comprises two distinct polymers of α -D-glucopyranoside. The linear polymer, amylose, is composed of several hundred glucose units connected by α -D-(1–4) glucosidic linkages (Fig. 16.7a). The branched chain polymer, amylopectin (Fig. 16.7b), is of much higher molecular weight and contains between 10,000 and 100,000 glucose units. The segments between the branched points contain about 25 glucose units joined as in amylose, while the branched points are linked by α -D-(1 \rightarrow 6) bonds. Most cereal starches contain about 75% amylopectin and 25% amylose.

Because amylose has straight chains, its molecules can approach each other within molecular range to form hydrogen bonds. This interaction is so strong that amylose can scarcely be dispersed in water. Amylopectin, on the other hand, has branched chains that have difficulty approaching each other, and it is therefore readily dispersed.

If starch, which is an amylose/amylopectin mixture, is dispersed in water, a gel results that forms a “skin” on standing. The skin is a result of hydrogen bonding. So-called waxy starches, such as waxy maize starch, which arose from genetic experimentation, are very high in amylopectin, and consequently they form gels that do not “skin.”

Amylose is prevented from skinning if it is converted into a derivative such as the phosphate. Phosphorus oxychloride or sodium trimetaphosphate are the reagents for phosphorylation. Only a small number of phosphate groups per polymer-molecule are

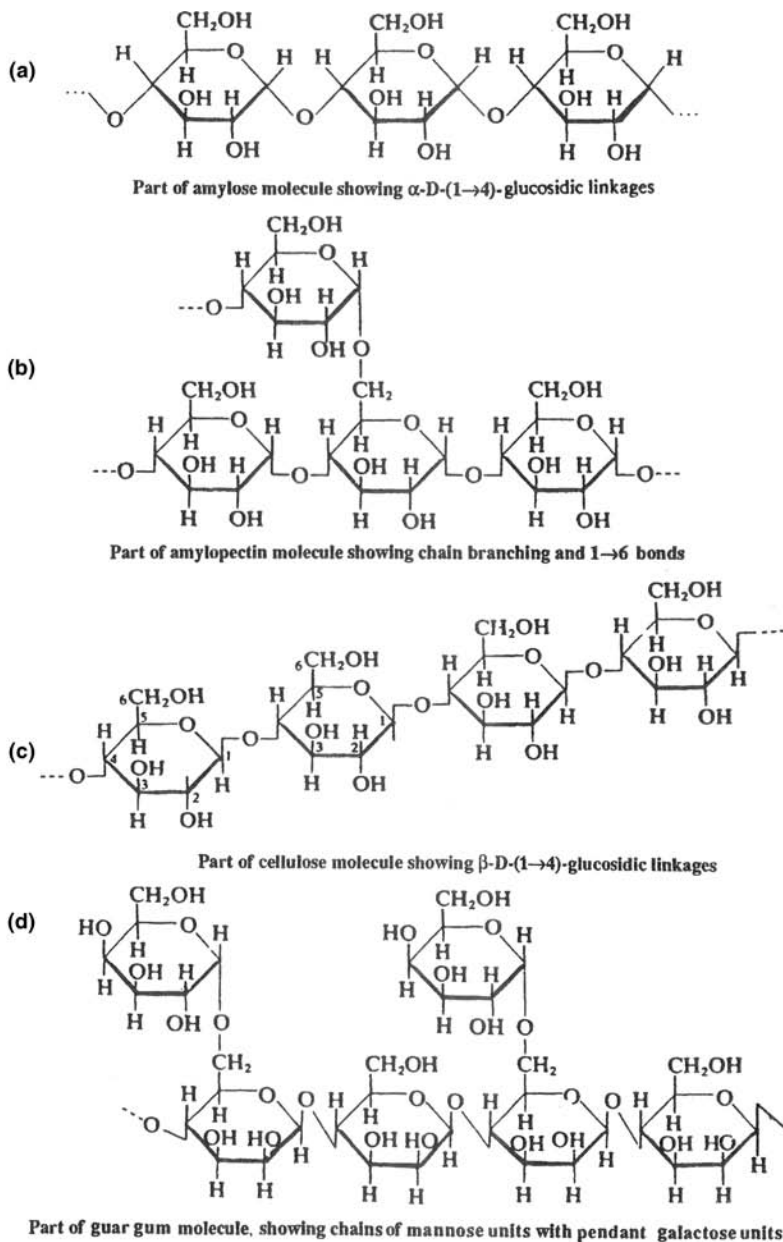
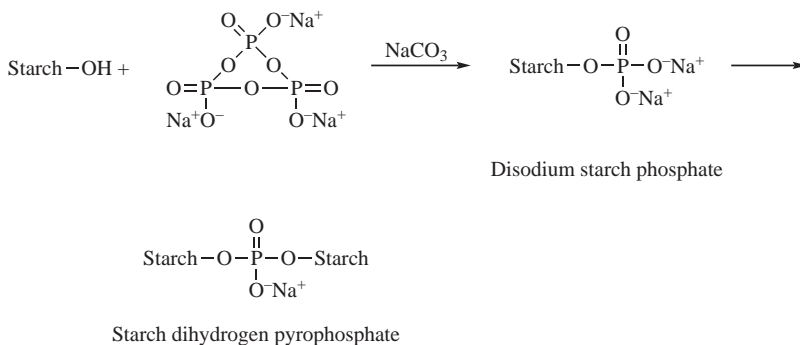


FIGURE 16.7 Starch, cellulose, and guar structures.

required to interfere with the hydrogen bonding. Consequently, starch phosphates are widely used as thickeners in the food industry and in other applications where a stable, high viscosity starch paste is required.



Other crosslinking agents for starch are also approved by the FDA, the most widely used being epichlorohydrin and linear mixed anhydrides of acetic and di- or tribasic carboxylic acids.

Starch is used in adhesives and as a size in textiles and paper manufacture. Sizing is a method for altering the surface properties of paper fibers. For example, many grades of paper are coated with an aqueous suspension of pigments (such as clay) with adhesives (such as starch) to provide a smoother surface, control the penetration of inks, and generally improve the paper's appearance. Dextrinized or degraded starch is used as an adhesive.

Starch acetates are made from starch and acetic anhydride, the extent of acetylation being measured by the degree of substitution (DS). This is the number of hydroxyl groups per glucose unit that is esterified. Total substitution therefore represents a DS of 3. Acetyl starches are used in the food, paper, and textile industries.

Hydroxyethylstarch, made by the action of ethylene oxide on starch, is used in paper coating and sizing, because it disperses more easily than starch itself and provides a dispersion of better clarity. Starch may also be reacted with cationic reagents such as dimethylaminoethyl chloride to give "cationic starch," which is used to impart greater strength to paper products. Acrylonitrile may be polymerized onto a starch polymer with the aid of a ceric sulfate catalyst to give a graft copolymer, which, on partial hydrolysis of the nitrile groups, is capable of absorbing large amounts of water (Section 6.4).

There are many other chemically modified starches that find specialized uses in the food industry but which are outside the scope of this book.

16.4 CELLULOSE

Cellulose is the primary substance of which the walls of vegetable cells are constructed. It occurs in plants, wood, and natural fibers, usually combined with other substances such as lignin, hemicellulose, pectin, fatty acids, and rosin. It accounts for about 30% of all vegetable matter. It may be represented by the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$.

Cellulose is a linear polymer composed largely of glucose residues in the form of anhydroglucopyranose joined together by β -glucosidic linkages (Fig. 16.7c). The β -linkages make the cellulose molecule very stiff compared with amylose, which has α -glucosidic linkages. It also makes cellulose more difficult to hydrolyze than starch. It is this difficulty that makes cellulose indigestible by humans. Accordingly, one of its uses is in diet foods, providing bulk and satiety but not calories. Had nature not insisted on β -linkages, a vast source of nutrition would be available to humans. On the other hand, cellulose with α -linkages would not be stiff and would not possess the structural properties it has in wood or the strength it has in textiles. Cows and other ruminants (broadly those that are accepted by Jews as kosher) have digestive systems containing organisms with enzymes that hydrolyze cellulose, and they are therefore able to use grass and similar materials for food. It is a slow process all the same, and the average cow has time for little else.

Cellulose may be obtained from wood or derived in very high purity from cotton linters (see below). The majority of production is used in paper manufacture. Cellulose also has a range of chemical uses. Cellulose derivatives (Fig. 16.8) may be water-soluble like methylcellulose, hydroxyethylcellulose, or sodium carboxymethylcellulose, or water-insoluble like the cellulose esters and ethylcellulose.

Methylcellulose, sodium carboxymethylcellulose, and hydroxyethylcellulose are all thickening agents and form protective colloids. For example, they are used in water-based latex paints to produce desirable flow and viscosity and to help stabilize the emulsion and pigment dispersions. Protective colloids affect the washability, brushability, rheological properties, and color acceptance of a paint. The same properties make them useful in foods, such as ice cream, and in inks and adhesives.

Methylcellulose is also used as a base for paper coatings since it is a good film former. Hydroxyethylcellulose is an adhesive and a binder in woven fabrics. Sodium carboxymethylcellulose (CMC) has a major use as a soil suspending agent in detergents, for if it were not present the dirt would tend to redeposit on the articles being washed. Instead, the CMC forms a protective colloid and holds it in suspension.

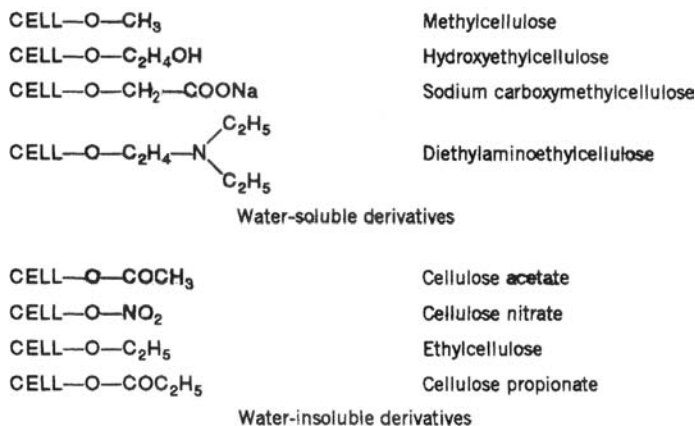


FIGURE 16.8 Cellulose derivatives. (Cellulose is represented as CELL—OH).

CMC is used in textile sizing, paper coating, and in oil well drilling mud, a material that helps to bring to the surface the dirt and rock particles dislodged by the drill. Diethylaminoethylcellulose is a cationic material useful in cotton finishing.

Sodium carboxymethylcellulose is made by spraying powdered cellulose first with sodium hydroxide solution and then with chloroacetic acid. The product contains some sodium chloride, which is removed by washing if food grade material is required. The commonest grade has a degree of substitution of 0.7 (0.7 hydroxyl substituted per glucose unit).



Cellulose

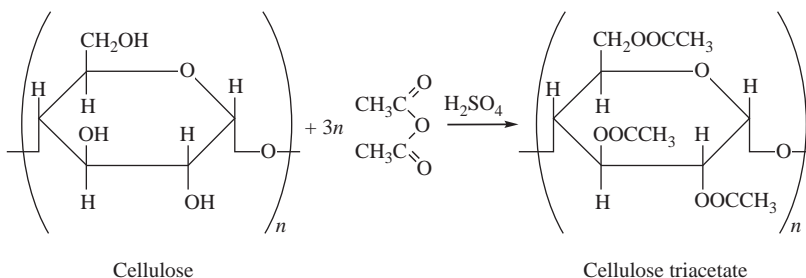


Sodium chloroacetate

Carboxymethyl cellulose

Its most important use is as an antisoil redeposition agent in detergents. As such, it prevents soil from redepositing on the textile surface once the surfactant has removed it. It is also used as a thickening agent in diet and other foods, where a higher viscosity is seen as desirable.

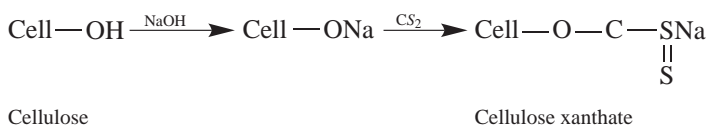
Cellulose triacetate is made by the action of equal quantities of acetic anhydride and glacial acetic acid on “chemical cotton,” a form of cellulose obtained by purification and conversion of cotton linters. All three hydroxyl groups in each glucose unit are acetylated.



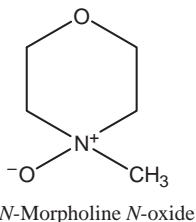
Cellulose acetate is obtained by partial hydrolysis of cellulose triacetate with water and a small amount of acetic and sulfuric acids. Addition of a large excess of water at the appropriate stage stops the hydrolysis and precipitates the acetate (with an average of two acetyls per glucose unit) as flakes. Cellulose acetate and triacetate may be used as plastics molding materials or spun into fibers and used for textiles. Cellulose triacetate is more difficult to process than the acetate but can be heat-set to give wash-and-wear fabrics. The largest use for cellulose acetate, however, is for cigarette filters. Cellulose propionate, acetate-propionate, and acetate-butyrate are also used as plastics materials and for films and lacquers. Ethylcellulose is useful in coatings and some plastics applications.

Cellulose nitrate or nitrocellulose was an early explosive (guncotton), as well as a plastic (celluloid), and surface coating (lacquer) both for wood and metal. Thus it was the first material used for coating automobiles by assembly-line procedures, its rapid drying making semiautomated production possible. It is also used in plastic moldings and film, and for fabric coating. Cellulose nitrate-coated fabric was widely used for airplane wings in the early days of aviation. As the basis for lacquers for furniture, it has largely been displaced by “melamine precatalyst” formulations. It is obtained by nitration of cellulose, about two nitro groups per glucose unit being introduced.

In addition to chemical conversion, cellulose may be altered physically or “regenerated.” Two processes are used, both of which start with highly purified cellulose from wood pulp. The products are known as viscose rayon and cuprammonium rayon. Viscose rayon was the first synthetic fiber to be produced commercially, and was launched by Courtaulds in 1905. It is produced by conversion of the cellulose into the soluble xanthate. It is first “ripened” with concentrated sodium hydroxide and then treated with carbon disulfide:



Thus 0.5–0.6 xanthate group per glucose unit is inserted. The solution is known as “viscose.” It is extruded through a spinneret – a metal disk with many tiny holes – into an acid coagulating bath, which regenerates the cellulose as a fiber. The fibers are washed and spun, that is oriented by stretching. The carbon disulfide is also regenerated and is recycled. The xanthation serves to solubilize the cellulose into a form from which it can readily be regenerated. During the regeneration, additional hydrogen bonds form, thus increasing strength. In all processes involving cellulose xanthate, the carbon disulfide is recovered and recycled. Total recovery is difficult, and there are pollution problems. An economic replacement has long been sought, and a brave attempt was the Lyocell process. Cellulose is dissolved in *N*-methylmorpholine *N*-oxide, not converted to a derivative as with rayon:



The solution is then extruded into water through a spinneret and the fibers spun into a product known as Tencel. It came onto the market in 1991. Courtaulds spent an enormous amount of money developing it and obtaining the patent, but it was not a

huge success. Courtaulds ran into financial difficulties and was taken over by Akzo. Tencel is now made by in Germany by Lenzing AG, which stresses its ecological benefits. Ionic liquids (Section 19.6) may be another way forward.

The premium cuprammonium rayon is made by dissolution of cotton linters or wood pulp in ammoniacal copper oxide. The solution is extruded through spinnerets into an acid bath in the same way as viscose. Cuprammonium rayon is chemically similar to viscose rayon but gives a finer yarn that is used in sheer fabrics.

Less vigorous treatment at the pulping stage leads to higher molecular weight cellulose, which yields so-called polynosic rayon with longer, finer fibers and high wet strength.

Cellophane film is also made from viscose solution, but the cellulose is regenerated in sheet form instead of fibers. It has high moisture transmission and is lacquered with a waterproofing agent, traditionally cellulose nitrate, which also imparts heat sealing capability. Poly(vinylidene chloride) is now widely used for this purpose. Cellophane is still a major packaging film for decorative items such as flowers and candy boxes, despite the advent of plastic films such as polyethylene, Saran, and oriented polypropylene.

Cellulose sponges are also made from xanthate, which is cast into blocks together with sodium sulfate crystals of various sizes. The xanthate is decomposed to regenerate cellulose, and when the sulfate is washed out it leaves holes in the sponge. Recovery of sodium sulfate is a major part of the operation.

The strength properties of cellulose, and to a degree its ability to hydrogen bond, make it useful for the formation of paper and nonwoven fabrics. For paper, cellulose is “beaten” or “pulped” until very finely divided particles result. Glassine is prepared from particles so finely divided that it is translucent. Opaque papers result from less finely divided particles. The wet and dry strength, bulk density, water and oil resistance, and gas permeability of paper are properties that can be modified either by adding chemicals to the pulp or by coating the finished sheet. Urea-formaldehyde and melamine-formaldehyde resins increase wet strength. Starch and rosin soap are widely used for sizing.

Nonwoven fabrics result when rayon is chopped into very fine particles known as fibrils and converted to sheets by various processes including (with the aid of a bonding agent such as an acrylate) the paper-making process.

16.4.1 Miscellaneous Chemicals from Wood

Wood was originally converted to chemically useful substances by destructive distillation. This involved heating the wood above 100°C to drive off water, followed by further heating above 270°C in the absence of air. The main product was charcoal, which was useful in steelmaking. One ton of hardwood gave about 270 kg charcoal. The liquid products, known as pyroligneous acid, contained about 50 kg acetic acid, 16 kg methanol, and 8 kg acetone plus 190 kg soluble tars and 50 kg insoluble tars. It is astonishing that, before the First World War, this yield of less than 1% was seen as an acceptable source of acetone (Section 6.7) and it was the only source of industrial methanol.³² Destructive distillation of pinewood also gave terpenes and hence turpentine.

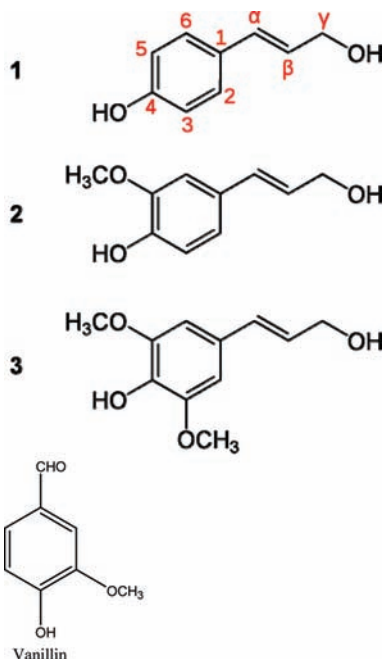


FIGURE 16.9 Vanillin and three common monolignols: (1) paracoumaryl alcohol, (2) coniferyl alcohol, and (3) sinapyl alcohol.

Wood is a composite of cellulose, hemicelluloses, and lignin approximately in the ratio 2 : 1 : 1. Almost pure cellulose is extracted from it by the Kraft process, in which wood chips are cooked for several hours at 130–180°C with sodium hydroxide and sodium sulfide. The process destroys most of the lignin and hemicelluloses, converting them to soluble fragments. The by-products are hydrogen sulfide, methyl mercaptan, dimethyl sulfide, turpentine, and tall oil (Section 15.3). Mechanical pulping, on the other hand, gives an inferior cellulose, but preserves the lignin.

Cellulose can be used as such for papermaking or converted to chemicals as described above. It can be hydrolyzed to glucose and thence to bioethanol as described below. The dimethyl sulfide can be oxidized to the aprotic solvent dimethylsulfoxide. Hemicelluloses have few uses and are added to animal feed. They are polysaccharides consisting of chains of mixed sugar residues, the most abundant being xylose.⁶

Lignin is an amorphous, crosslinked three-dimensional polymer made up of phenylpropane polymers and hydrolyzed by alkali during the Kraft process for papermaking. Three of these together with vanillin (see below) are shown in Figure 16.9. Figure 16.10 shows part of the lignin structure and some of the products that a U.S. Department of Energy report feels might be made from it. The report produces literally hundreds of possibilities but scarcely any of them are currently commercialized. Key problems are solids handling, fractionation of feedstocks and

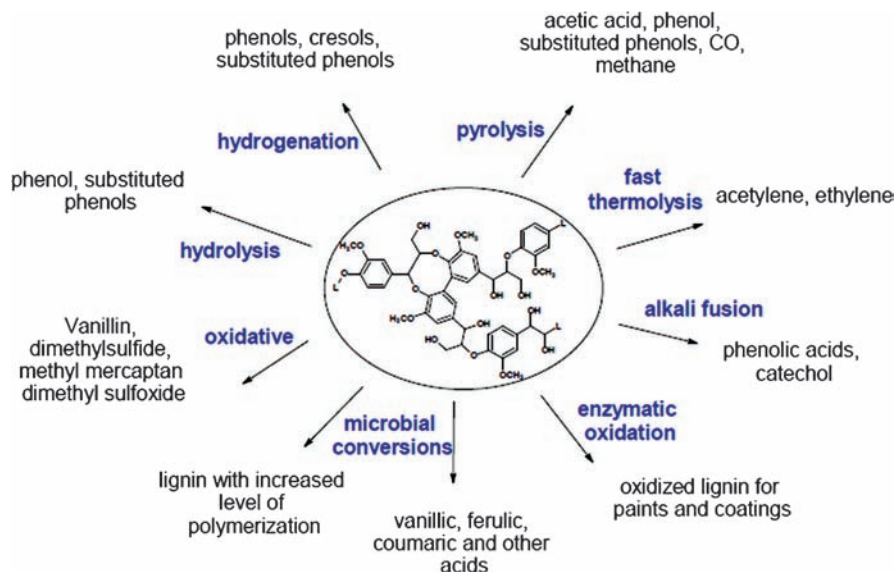
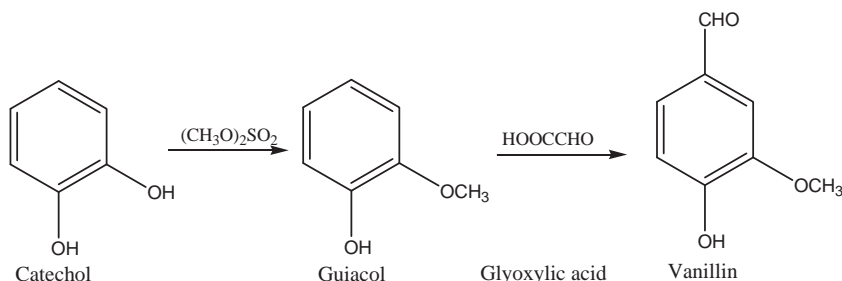


FIGURE 16.10 Chemicals from lignin. (Source: J. E. Holladay, J. F. White, J. J. Bozell, and D. Johnson. Top value-added chemicals from biomass, U.S. Department of Energy; <http://www1.eere.energy.gov/biomass/pdfs/pnnl-16983.pdf>.)

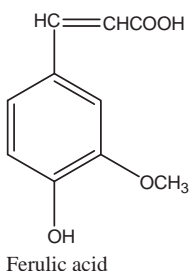
products, and coproducts resulting in the wrong amounts for the market. We shall confine ourselves to two lignin-based products, one currently produced and the other typical of the types of chemistry that might be of value.

16.4.1.1 Vanillin

Natural vanillin is extracted from the seed pods of *Vanilla planifolia*, a native to Mexico, but now grown generally in tropical areas, with Madagascar as the largest producer. Only 1800 tons/year is available, and the demand is approximately 12,000 tons. Some is extracted from the lignin wastes after wood pulp has been extracted with alkali in the Kraft papermaking process. That is the reason for its listing here. In recent years, however, the majority has been made synthetically from guaiacol and glyoxylic acid. Guaiacol can be isolated from guaiacwood oil or by oxidation of lignin but methylation of catechol, for example, with potash and dimethyl sulfate, is preferred.⁷

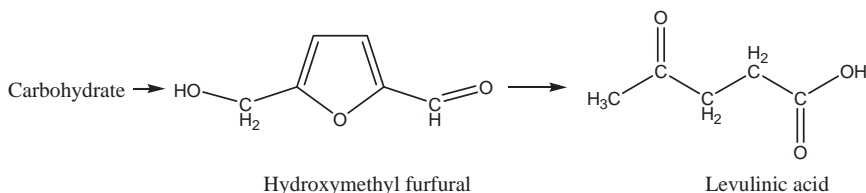


Rhodia makes vanillin from the action of microorganisms on ferulic acid. The route is much more expensive, but Rhodia sells it as a “natural” product at a premium price.⁸

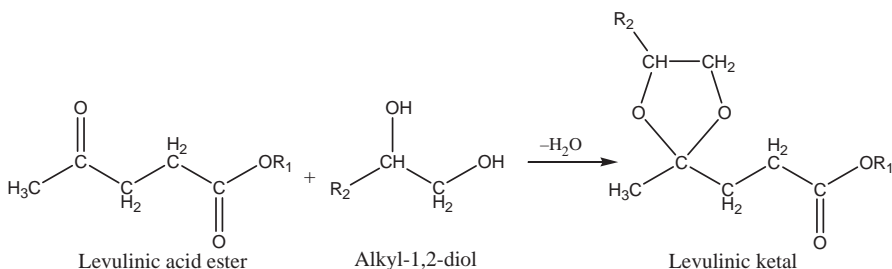


16.4.1.2 Levulinic Acid

Levulinic acid is a five carbon building block derived from agricultural wastes by acid and thermal decomposition. Carbohydrates apparently go through glucose and fructose to hydroxymethylfurfural and then to levulinic acid, although the route is by no means obvious:



Levulinic acid is one of the Department of Energy's chosen building blocks (see below). The Office of Industrial Technologies suggests that use of levulinic acid at 90,000–180,000 metric tons/year levels could save 75.6 trillion Btu/year of energy by 2020, reduce waste by 26.2 million metric tons per year, and generate annual cost savings of \$3.5 billion per year. It can be converted to acrylic and succinic acids, pyrrolidones, and diphenolic acid, a potential replacement for bisphenol A in polycarbonates (Section 9.1.2.2). More applications result from its combination with diols to give L-ketals⁹:



Segetis, a Minnesota company, is currently operating a 100 metric ton/year pilot plant aimed at replacing phthalates as PVC plasticizers.

16.5 GUMS

Gums, like starch and cellulose, are carbohydrate polymers. They differ from them in that the monomeric unit may be a sugar other than glucose, and the chemical configuration and the way in which the units are joined are different.

The molecular weight of gums is usually between 200,000 and 300,000, that is, about 1500 monomer units. Guar (Fig. 16.7d) is a typical gum. It consists of a chain of mannose units joined by 1,4-glycosidic linkages, and attached to every other mannose unit is a pendant galactose unit.

The main gums and their origins are shown in Table 16.1. Each gum has characteristic properties slightly different from other gums. Frequently, the commercially important differences lie in the rheological properties of the dispersions of the gums in water. Gums may be chemically modified just as cellulose is, and the most useful derivatives are carboxymethyl, hydroxypropyl, and dimethylaminoethyl gums.

The applications of gums are wide. Guar gum is the most important and may be considered typical. It has many times the thickening power of starches and may be used in combination with them. Its derivatives are useful as flocculants for precipitating mineral slimes and as a suspending agent for ammonium nitrate that not only leads to a much cheaper explosive than dynamite or nitroglycerin, but also to one that is more effective, because it assumes the shape of the cavity where the blast is to start.

Carboxymethylguar gum is an anionic material useful as a print gum paste. This means that it serves as a binder for a pigment used to impart color and design to cloth. In contrast, diethylaminoethylguar gum is cationic and is used in paper manufacture. It is a particularly effective flocculent of “fines,” the very fine cellulose particles in the paper matrix, onto which it adsorbs. By helping to retain the “fines,” it increases the yield of product and, since fewer “fines” are in the water that drains from the machine, the pollution problem is diminished. Guar itself strengthens the paper by hydrogen bonding to the fibers and helping them achieve a linear rather than a random configuration.

TABLE 16.1 Natural Gums

Source	Examples
Plant seeds	Guar gum, locust bean gum
Seaweed extracts	Alginates, carrageenan, agar
Tree exudates	Gum arabic, karaya gum, gum tragacanth
Citrus fruits	Pectin
Animal skin and bones	Gelatin
Fermentation	Xanthan gum

Xanthan is an unusual gum in that it is obtained not from animals or plants but by fermentation of carbohydrates with a bacterium, *Xanthamonus campestris*. The gum is a complex glucose polymer, and its aqueous solutions are unusually stable – showing unchanged viscosity over broad temperature, salt concentration, and pH ranges. The product is therefore used to thicken oven cleaners based on strong alkali as well as the acid solutions used as metal cleaners. Differently formulated, it is a component of low-calorie salad dressings. Its largest use is as a component of oil well drilling mud that must contain saline water. Its largest potential use is in so-called enhanced oil recovery where it thickens the water used to “push” oil, unobtainable in any other way, through the dense, oil-bearing rock formation. Unlike other gums such as guar, xanthan does not adhere to surfaces. If it did, it would deposit as a film on the rock surface and lose its thickening power.

16.6 FERMENTATION AND BIOTECHNOLOGY

When supplied with suitable nutrients, single cell microorganisms, yeasts, molds, fungi, algae, and bacteria, including the important antibiotic-producing *Actinomyces*, thrive and multiply. As they do so, various waste products of their metabolisms accumulate. The microorganisms can tolerate only low concentrations of their own wastes. Nonetheless, under certain circumstances, these wastes, which can be either intra- or extracellular, can be concentrated and used. The process is known as microbial conversion or fermentation, and it occurs as a result of the catalytic action of various enzymes produced by the microorganisms on the nutrient or substrate. Thus fermentation can also be brought about by pure enzymes or portions of cells that contain enzymes such as mitochondria.

The substrate is usually but not always a carbohydrate. In the past, there was interest in the use of gas oil or other petroleum hydrocarbon substrates for the production of single cell protein for both human and animal food. Much of the development work was done in the days of seemingly abundant petroleum with ammonia added as a nitrogen source. In the presence of aqueous nutrient salt solutions containing inorganic sulfur, phosphorus, and nitrogen, a variety of *Pseudomonas* will grow to give a bacterial culture, where the dried cells contain up to 81% protein. This is supplemented by various essential amino acids that are underrepresented in single cell protein and used as animal feed. ICI built a 60,000 metric ton per year methanol-based plant, which opened in 1979. It turned out not to be economically viable, partly because of the rise in oil prices.

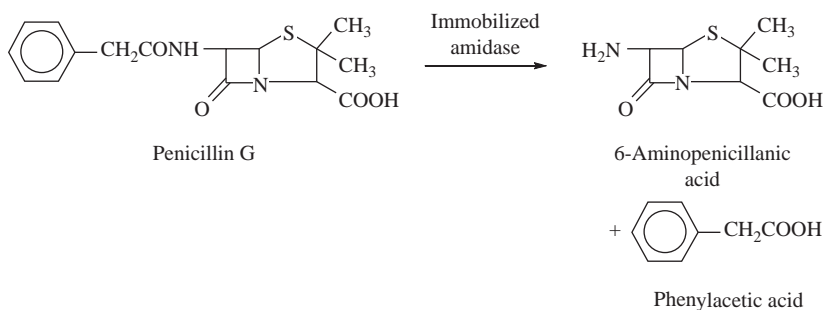
The plant was sold in 1985 to Marlow Foods, a joint venture of ICI and Rank-Hovis-McDougall, for production of mycoprotein – a relation of the mushroom – which can be processed to yield a proteinaceous food with the fibrous texture of meat. The product is known as “Quorn.” It is marketed especially to vegetarians. With the dismemberment of ICI, it eventually passed in 2005 to Premier Foods, which, in October 2010, was said to have received an offer from another food company. A joint venture of Phillips Petroleum and Petrofina also produced specialty proteins for human consumption but it was sold to Monsanto in the late 1990s.

In the United States, inexpensive soy protein is available, and there is little incentive for the development of other sources. Soybean production is also being expanded in Brazil, and there should be adequate supplies of vegetable protein in the Western Hemisphere for the foreseeable future. On the other hand, there are many protein-short countries in the world where fermentation protein might be helpful, and there is believed to be a plant in the Russian Federation.

Fermentation is used in the chemical industry only when an economical chemical process is not available. Its largest volume application is in sewage treatment, where obnoxious amines and sulfur compounds in the sewage are oxidized to nitrates and sulfates. Other wastes are anaerobically digested to methane or aerobically oxidized. The next largest application is the production of alcoholic beverages, where the product can either be consumed in dilute form (beer and wine) or concentrated by distillation (whisky, brandy, gin, vodka).

Fermentation reactions are usually selective and take place under mild conditions. "Waste heat" from power stations, refineries, and factories can easily be used as an energy source if one is required. On the other hand, nutrients are frequently expensive, reactions are slow, and the product is so dilute that huge tank capacities are required. Unless the product precipitates (e.g., single cell protein), its isolation can be tedious and expensive. If the fermentation is aerobic, mass transfer of oxygen to the required site demands intricate engineering. Contrary to popular opinion, fermentation processes are not ecologically friendly. In general, they produce large volumes of waste water and mycelium with a high biochemical oxygen demand, which must be treated before discharge into a waterway. Nonetheless, there are products for which fermentation methods are uniquely suitable.

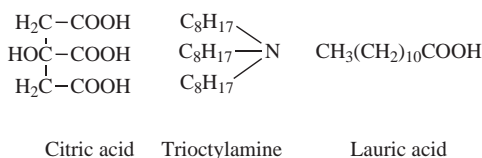
Antibiotics are an example. By definition, all antibiotics – penicillins, cephalosporins, macrolides, tetracyclines, and so on – are made by fermentation, but there are few pharmaceutical antibacterials made without a fermentation stage. Penicillin is made by fermentation of a corn-steep liquor substrate (a cheap form of sucrose) with *Penicillium chrysogenum*. For the production of semisynthetic penicillins, such as amoxicillin, the penicillin from this first stage is then cleaved to 6-aminopenicillanic acid with an immobilized amidase.



Penicillin has been synthesized in the laboratory but the process would be hopelessly uneconomic compared with the biotechnological route.

Lactic (Sections 16.1 and 19.12) and citric acids are made by fermentation. Citric acid has a structure that makes economical chemical synthesis difficult. It is obtained by growing *Aspergillus niger* on a molasses, starch, or hydrocarbon substrate.

One method for separation of the acid from the fermentation broth is unique. The mixture is shaken with a trioctylamine–lauric acid “couple” in an organic solvent. The citric acid displaces the lauric acid from the acid–base couple and enters the organic phase, leaving the impurities behind. After phase separation, the organic phase is shaken with hot water. The entropy of the phase transfer is such that, at the higher temperature, the process is reversed and the citric acid returns to the aqueous phase from which it can simply be extracted.



Of great interest is DuPont’s manufacture of 1,3-propanediol by fermentation of corn-derived glucose with a genetically modified organism.¹⁰ This is the raw material for the new polyester, poly(trimethylene terephthalate), trade name Sorona®. The new polymer is 37% by weight renewably sourced. It can be used in textiles, apparel, and packaging. Its initial application is in carpets, and large scale supplies made by the new process became available in 2009. It uses less energy, reduces emissions, and provides a premium product.

Metabolic Explorer, a technology development company, aims to develop “cell factories” for bulk chemicals and are working with the French Roquette Frères to produce 1,3-propanediol, 1,2-propanediol, *n*-butanol, L-methionine, and glycolic acid from carbohydrate feedstocks.¹¹

The Weizmann process, which gives acetone and *n*-butanol by fermentation of corn with bacillus *Clostridium acetobutylicum*, was important in World War I, when Britain was in desperate need of acetone for the gelatinization of cordite, a smokeless explosive. The yield was only 8% acetone and 16% butanol, but Britain was desperate. Weizmann’s discovery had political as well as military and scientific implications¹² but the process itself was displaced by petrochemicals.

Biobutanol, however, is potentially a better fuel than ethanol. It gives 88% of the mileage per liter of gasoline compared with ethanol’s 70%. It is less prone to water contamination and less corrosive to pipelines. BP/ABF Foods at Hull are trying to increase yields and are considering a pilot plant alongside their \$400 million bioethanol plant at Hull, United Kingdom, which came on stream in 2010. DuPont, British Sugar, and various other companies are working along similar lines.

GEVO (Englewood, Colorado) uses a genetically modified organism to produce isobutanol (2-methylpropanol) from the sugars derived from cellulosic biomass. Isobutanol can be dehydrated to isobutene and dimerized to gasoline. It is claimed that

it works better than Weizmann's *Clostridium acetobutylicum*.¹³ There seems to be a collaboration with BP in England, where a bioethanol/biobutanol plant is already on stream.

In addition, Scotch whisky distilleries have found that two main waste products from whisky distillation – a liquid called pot ale, and draff, the residue of husks after fermentation of the grain used in brewing – are rich in butanol. This can be extracted and used as biofuel. Serious whisky drinkers can now feel that they are contributing to renewable “green” chemistry.

Other noteworthy fermentation processes include the production of evening primrose oil (Section 15.3); the use of an immobilized cell to hydrolyze acrylonitrile to acrylamide (Section 6.11.3); the production of vitamin C (Section 16.1); the 11-hydroxylation of progesterone in the synthesis of cortisol¹⁴; and the production of synthetic cocoa butter (Section 15.12.1).

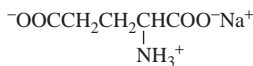
A route to hydroquinone from glucose has been reported but does not yet appear to have been commercialized.¹⁵

16.6.1 Amino Acids

The synthesis of L-amino acids by fermentation has been pioneered largely in Japan. Production of every essential amino acid by fermentation is now possible. Because demand is small, many of them are still being made by chemical methods followed by resolution of the resulting DL-racemate. The most important amino acids made by fermentation are L-glutamic acid, L-lysine, L-arginine, and L-aspartic acid.

16.6.1.1 L-Glutamic Acid

L-Glutamic acid is produced by fermentation of glucose or sucrose from molasses or other sugar refinery wastes. The bacterium is *Micrococcus glutamicus*, and nitrogen is supplied in the form of ammonia. Monosodium glutamate is used as a flavor enhancer in prepared foods, such as packaged soups. Only the L-form enhances flavor. Monosodium glutamate is also widely used in Southeast Asia and in Chinese restaurants throughout the world. Excessive doses can lead to *Kwok's disease*, the so-called Chinese restaurant syndrome.

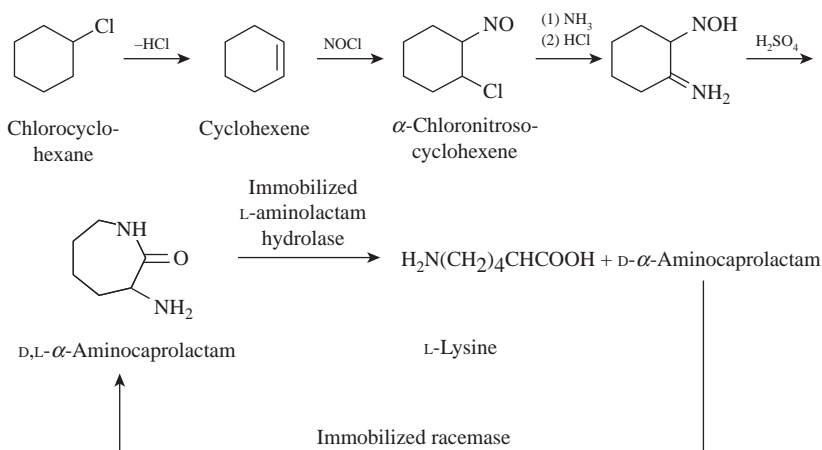


Monosodium glutamate

16.6.1.2 L-Lysine

Lysine was originally manufactured by DuPont, which used a conventional synthetic route followed by classical resolution of the D and L isomers. It was also isolated from blood meal by General Mills Chemicals. The L-form resulted, obviating the need for the tedious resolution. These methods were displaced by fermentation routes based on *Clostridium glutamicum* and ammonium acetate or carbohydrate/ammonia

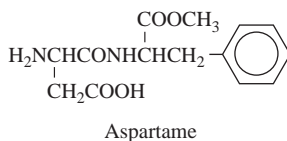
substrates. Toray then developed a new route based on the nitrosyl chloride chemistry and the chlorocyclohexane by-product from its caprolactam synthesis (Section 9.2.2).



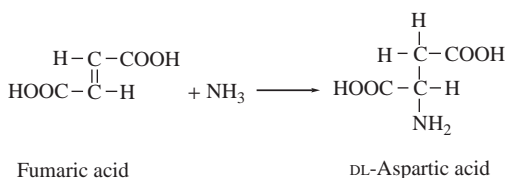
Only the L- α -aminocaprolactam is attacked by the L-hydrolase, so that only L-lysine is produced. The D- α -aminocaprolactam is racemized to a D,L-mixture for reuse, with the aid of a second immobilized enzyme.

16.6.1.3 L-Aspartic Acid

L-Aspartic acid is an amino acid with wide uses in the food and pharmaceutical industries. Its significance on a tonnage scale arises because it is a starting material for the nonnutritive sweetener Aspartame[®].



The enzyme *aspartase* promotes the addition of ammonia across the double bond of fumaric acid to give the L-form of aspartic acid:



Microbial strains of *E. coli* with high *aspartase* activity are immobilized in a κ -carrageenan gel crosslinked with glutaraldehyde and hexamethylenediamine and

operate at a temperature of 38°C. κ -Carrageenan is a gel-forming mixture of sulfated polysaccharides extracted from red seaweed.

16.6.1.4 L-Cysteine

L-Cysteine is used as a flavor enhancer in foods and with potassium bromate and ascorbic acid in the ADD (Activated Dough Development) process.¹⁶ This is a method of producing so-called no-time doughs, designed to reduce the long fermentation periods required in the traditional bread-making process. L-Cysteine is a fast-acting reducing agent, which aids the fission and reformation of disulfide linkages in the gluten, easing the expansion of the dough. Bromate is considered a grade 2B carcinogen by the International Agency for Research on Cancer and banned in the United Kingdom, Europe, and some other countries but still permitted in the United States.¹⁷ The reason is that it is destroyed at baking temperatures. The FDA currently permits the addition of potassium bromate in flour provided that its inclusion does not exceed 0.0075 part for each 100 parts of weight of the flour (or 750 parts per million).¹⁸

Bizarrely, until 2001, L-cysteine was manufactured from the α -keratin found in hair and feathers or by racemic separation of DL-cysteine. The latter was obtained by a demanding three-step process (Bucherer–Bergs reaction), involving hazardous reagents like chloroacetaldehyde, hydrogen sulfide, and hydrogen cyanide. The Chinese were widely believed to use human hair, raising questions as to whether this was cannibalism and whether the product was *kosher* or *halal*. It was certainly *natural*, but this did not seem to be a selling point. The Japanese food company Ajinomoto then commercialized a chemical route (Fig. 16.11) starting with methyl acrylate, which is chlorinated to α -chloromethyl acrylate. Reaction with thiourea gives racemic aminothiazolyl carboxylic acid (ATC). In a one-step microbiological process with a genetically modified enzyme this is then converted to L-cysteine. The D- and L-ATC are kept in equilibrium by an ATC racemase, so that eventually all the racemic ATC is converted to the L-product. Three enzymes of *Pseudomonas thiazolinophilum* are involved in partial steps of the biotransformation.¹⁹

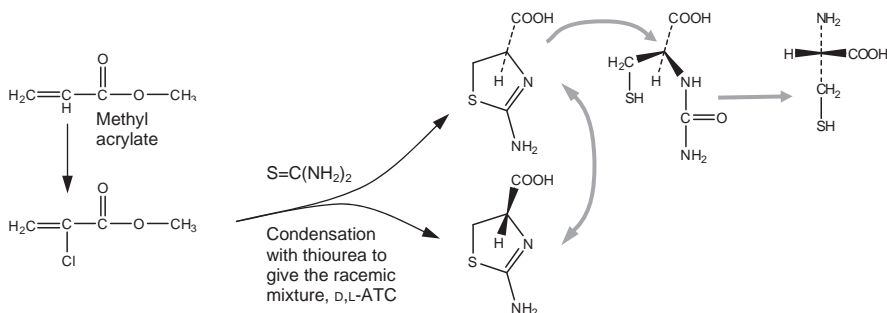
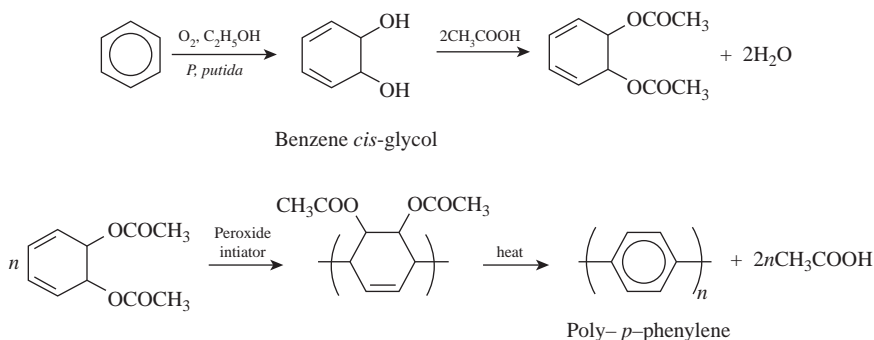


FIGURE 16.11 Ajinomoto synthesis of L-cysteine.

16.6.2 Polymers

A fermentation route to nylon 66 is described in Section 9.2.1. The production of xanthan gum (Section 16.5), which has a molecular weight of more than a million, is an example of the production of polymers by fermentation but the product does not have the physical properties generally associated with plastics.

ICI developed a route to a biodegradable polyester copolymer of γ -hydroxybutyric and γ -hydroxyvaleric acids, which was later sold to Monsanto and then to Metabolix, discussed further in Section 19.12. ICI also developed a fermentation route to poly-*p*-phenylene. This polymer has excellent high temperature resistance and hydrolytic stability but is highly intractable with no known solvency, and it can be molded only at high temperatures and pressures. ICI found a strain of *Pseudomonas putida* that would convert benzene to benzene *cis*-glycol when supplied with benzene and ethanol in the absence of oxygen. Esterification with acetic acid leads to a diester, which is polymerized with a free radical initiator. The intermediate polymer is not aromatic. It can be solubilized and is converted into fibers and supported or unsupported film. Heating volatilizes the solvent and completes the polymerization to polyphenylene in situ. The acetic acid is regenerated for recycle. This ingenious process was never commercialized.



16.6.3 Proteins by Recombinant DNA Technology

The revolution in biotechnology over the past two decades has made possible the manufacture of almost any protein by recombinant DNA technology. Large scale single cell protein production has already been mentioned in Section 16.7. The technique by which protein-producing genes are spliced into single cell organisms is altogether remarkable. Insulin, interferon, a range of blood clotting factors for hemophiliacs, human growth hormone, bovine growth hormone, and a range of vaccines are already on the market. Organisms have already been cloned to produce others should it become economic. We can scarcely conclude this section on fermentation without mention of this development.

Implications for the heavy chemical industry, however, are less dramatic. The largest volume genetically engineered protein on the market is insulin, which sold in 2009 for about \$60 per gram. Annual production is measured in kilograms rather than tons. The adaptation of these methods to bulk proteins presents a whole series of new problems. On the other hand, genetically modified organisms are being used to make nonproteins such as polyalkanoates (Section 19.12) and isobutanol (Section 16.6).

16.6.4 Fermentation and Renewables Scenarios

There are many motives for investigating non-fossil-fuel-based routes to chemicals. There are political uncertainties, concerns about pollution and resource depletion, and worries about global warming, which make it desirable to manufacture chemicals in a carbon-neutral way from renewable feedstocks. That means biomass. An estimated 180 billion metric tons of biomass grows annually of which 75% is carbohydrates. These are not only wood but also sorghum, wheat, potatoes, bagasse, corncobs, agricultural wastes, and switch grass, which is said not to require fertilizer. Only 4% of these carbohydrates are used by people; the rest decay, rot, and recycle. All of these products can be converted to synthesis gas, and that is currently the fate of many. Meanwhile, in 2004, the U.S. Department of Energy published a shortlist of twelve carbohydrate-derived building blocks that could represent a platform for a so-called biorefinery – a carbohydrate-based equivalent of a petroleum refinery. These are shown in Table 16.2. In general, they are produced at present in only small quantities but they offer opportunities for the future. We have discussed some of them already, along with the products that are already established industrial chemicals.

Discussion of fermentation, however, raises the question as to whether the chemical industry could survive if supplies of oil and natural gas were depleted. In terms of technology, the answer is encouraging. In between the world wars, fermentation was a major route to organic chemicals, providing ethanol, *n*-butanol, and acetone as feedstocks. Production was expensive and tonnages were low. Today, reaction pathways exist by which most modern organic chemicals and polymers could

TABLE 16.2 Department of Energy's Top 12 Carbohydrate-Derived Building Blocks

1,4-Succinic, fumaric, and malic acids
Sorbitol
Glycerol
3-Hydroxybutyrolactone
Levulinic acid
Itaconic acid
Glutamic acid
Glucaric acid (saccharic acid)
Aspartic acid
3-Hydroxy propionic acid
2,5-Furan dicarboxylic acid
Xylitol/arabinitol

be made from these feedstocks more efficiently than they were 60–80 years ago. Thus ethanol can be dehydrated to ethylene. Indeed, in 2010, Braskem inaugurated the world's first large-scale fermentation ethanol-to-polyethylene operation. The 200,000 metric ton/year plant is in the Triunfo Petrochemical Complex, in Rio Grande do Sul, Brazil. Customers are apparently happy to pay a premium of up to 66% for the environmentally friendly product.²⁰ Ethylene can be dimerized to 2-butene, and the metathesis reaction (Section 4.14.1) then permits the production of two molecules of propylene from one each of ethylene and 2-butene.

That is not all. Glucose can be fermented by other organisms to 3-hydroxypropionic acid and lactic acid. 3-Hydroxypropionic acid dehydrates readily to acrylic acid for coatings and superabsorbents (Section 6.11.5). Lactic acid is a raw material for polylactate biodegradable polymers (Section 19.12). It is also valuable in the detergent industry, being a good descaler, soap-scum remover, and a registered antibacterial agent.

Thus C_2 , C_3 , and C_4 olefins basic to the chemical industry and various other useful feedstocks can be produced via fermentation but generally at an uneconomic cost. Indeed, there is a question as to whether ethanol is truly a renewable energy source. This is discussed in Section 16.6.5.1.

Methane is produced by anaerobic fermentation of sewage sludge and of organic wastes generally. About 75% of the calorific value of sludge can be recovered in this way, which sounds impressive but in fact serves mainly to make sewage plants independent of outside sources of power. In India and China, biomass fermentation processes are well developed and are used in rural areas to generate heating and cooking gas from accumulated biomass wastes. The so-called biogas, as indicated above, makes an important contribution to an improved lifestyle in these regions.

Nonfuel uses based on sugars and carbohydrates are also being investigated, some of which were mentioned earlier in this chapter. There have been many reports on the topic, for example, the Department of Energy Report, the DoE Lignin Report, the BREW Project Report, and the FROPTOP program.²¹

These reports provide references to various other reports and projects. They suggest routes from sugars, carbohydrates, and other renewable materials to a huge range of chemicals. Figure 16.12 gives examples, but the reports give much bigger and more complex diagrams that fare better as wall charts than as book illustrations. Figure 16.10 shows suggested chemicals from lignin, generally regarded as the least tractable of wood products. We should not sneer at these. Such is chemists' ingenuity that it is currently possible, by the expenditure of time and effort, to get from almost any chemical to any other. But there are problems. These are not only economic but also scientific. Synthetic routes are important, and the routes suggested look to be long and costly. But, in addition, separation processes are a problem. It is customary to tell first-year chemical engineering undergraduates a parable of the discovery of a miracle catalyst and reactor that will turn any cheap feedstock into the chemicals that industry requires in exactly the right proportions. The catch, of course, is that the problem of separating the reactor output is insurmountable. The miracle catalyst is useless.

In summary, therefore, fermentation is currently valuable to do what the chemist cannot do, such as antibiotic and L-amino acid production, and steps in vitamin C and

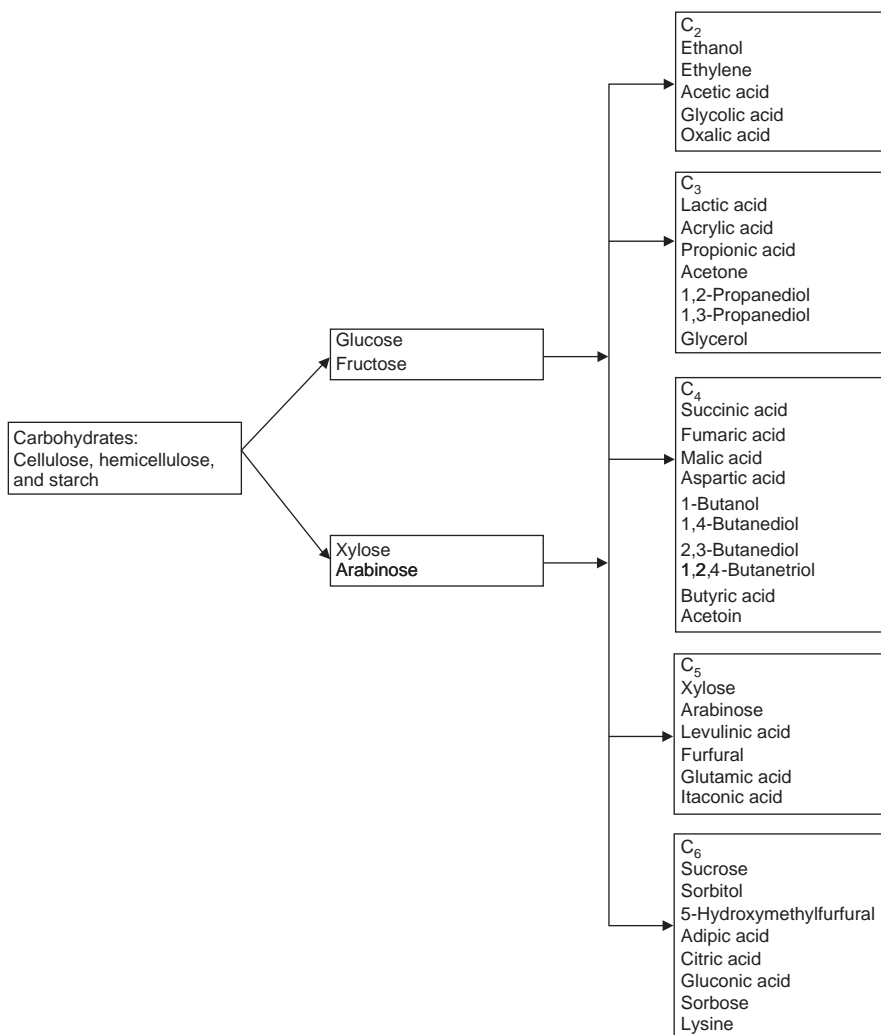


FIGURE 16.12 Possible chemicals from carbohydrates.

cortisone synthesis. It can provide energy via methane and has been the basis since biblical and classical times of bread and alcoholic beverages. At a cost, it can provide ethanol, which can be dehydrated to ethylene, on which a lion's share of the chemical industry is based. Renewable raw materials may well compete with food for land and fertilizers, although, again, they are valuable in specific cases. How much energy, food, or ethylene will be produced by fermentation or from renewables, however, depends on economics, which, in spite of some exceptions, tend to favor petrochemicals. Given the current level of fossil fuel reserves and allowing for the exceptions and for fuel uses, the situation is unlikely to change much in the next generation.

16.6.5 Biofuels

With the threatened long-term depletion of petroleum supplies and the wish to reduce carbon dioxide emissions there has been much discussion of the possibility of producing renewable fuels from crops.

Fossil fuels were derived from carbon, fixed over millions of years. “Peak” oil has not yet been reached, but is expected soon. Petroleum is a compact liquid feedstock, easy to transport and with a high intrinsic energy. It is polluting in terms of building up atmospheric carbon dioxide, and also in producing sulfur dioxide and nitrogen oxides. Natural gas is less and coal more polluting, but both with high intrinsic energy.

Biofuels contain carbon fixed by vegetation – plants, trees, microalgae – in “real time,” say, between 1 and 10 years. The carbon is recycled to the environment within a year or so of harvesting. There is a short-term increase in carbon dioxide, but otherwise biofuels are less polluting. Their drawback is that they require the exploitation of large land areas; they compete for land with food; they have lower intrinsic energy; and they involve solid feedstocks that are bulky and difficult to transport, and need to be liquefied rapidly near where they are harvested.

The biofuel industry has developed because of government mandates and short-term incentives. In the United States there is the Energy Independence and Security Act (EISA) and Renewable Fuels Standard (RFS). In the United Kingdom there is the Renewable Transport Fuel Obligation (RTFO). This requires $3\frac{1}{4}\%$ of all fuels sold to come from crops and the proportion is due to increase each year and to reach 13% by 2020. The mandate for 2010 imposed a 13 pence per liter penalty for noncompliance.

Liquid fuels for transport have the highest profile. Bioethanol is discussed below and biodiesel in Section 15.12.3.

16.6.5.1 *The Brazilian Experience*

Ethanol is the leading biofuel and, in Brazil, cars were designed that ran entirely on ethanol. Although Brazil’s was successful technically, its economics were poor in light of the low petroleum costs of the late 1980s. Collor, the president elected in 1989, campaigned on a platform that included phase-out of the alcohol program. Market interactions helped him, for the world price of sugar cane increased and many refiners chose to convert sugar cane juice to sugar rather than alcohol. By so doing, they created an alcohol fuel shortage, which caused Brazil to import alcohol to fuel its one million cars that could not operate on petroleum-based fuel. The Iraqi invasion of Kuwait caused a stunning reversal of both Collor’s campaign platform and the manufacture of sugar, because it caused the price of crude petroleum to increase to a point that the economics of Brazil’s alcohol fuel program became more reasonable and they have stayed that way. Gasohol is widely used in Brazil today, but cars that are dependent only on ethanol have been superseded by other cars (known as flexible fuel vehicles) running on a mandatory blend of gasoline and 25% ethanol. Brazilian ethanol production in 1975 was 320 million liters, rising to 12 billion in 1986. By 2009, it had risen to 24.9 billion liters (19.6 million metric tons) and represented 37.7% of world fuel ethanol. It was made from sugar cane. Brazil has the advantage that sugar cane has a higher carbohydrate content than American corn,

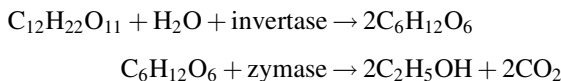
gives two crops a year and higher yields per acre. It grows fast and harnesses the sun's energy with a relatively high efficiency of about 8%.

16.6.5.2 *Is U.S. Bioethanol a Renewable Energy Source?*

In the United States, ethanol is used as an oxygenate in gasoline, because methyl-*t*-butyl ether has lost popularity (Section 7.2.1). Fermentation ethanol from corn starch was seen as a replacement, at any rate in the short term, although total use of ethanol à la Brazil was seen as a possibility. It would be much less economic than Brazilian ethanol from sugar cane and currently requires a huge subsidy. In addition, ethanol has a much lower octane number than MTBE and raises the volatility of gasoline to which it is added. It contains much less energy per unit volume than gasoline, and there is the previously mentioned concern of whether or not the ethanol from corn starch contributes more energy than its manufacture requires.

Corn growing increases degradation of agricultural land and depletes it of potassium, nitrogen, and phosphorus. Batch processes, such as fermentation, are less energy efficient than continuous processes and there is the problem of disposing of the waste water—about 6 kg per kg of ethanol—and the biomass. Thus the wisdom of using subsidized ethanol either as an oxygenate or as a pure fuel is doubtful. Furthermore, if all the corn, wheat, and other cereal crops grown by world farmers were converted to ethanol, it would still give only 6–7% of the energy equivalent of present world oil production.

The fundamental question, however, is whether ethanol is actually a renewable energy source. Does its production use more nonrenewable fossil fuel energy than is produced when it is burned? The production process starts with the farmers raising corn. They use agrochemicals (pesticides, herbicides, insecticides, etc.) and gasoline-powered tractors. The corn must then be harvested and the starch extracted in a complex process called wet milling. Next, it must be subjected to batch fermentation first to give sugars (sucrose, glucose, and fructose) and then to give a dilute aqueous solution of ethanol. That must be distilled. An immediately obvious drawback is that two out of the six carbon atoms per glucose unit are straightaway lost as carbon dioxide:



Straightforward distillation of the fermentation liquor gives an ethanol azeotrope containing 4.4% water—too much for fuel use. On the other hand, farmers are not set up to carry out the fermentation efficiently nor operate the azeotropic distillation with benzene on a farm scale, especially as benzene is toxic. Instead, their corn is purchased by companies like Archer-Daniels-Midlands, which extract the starch and so on and which get over 80% of the subsidy. The shipping of the corn and the complex distillation are energy intensive. Pimental²² has calculated that about 72% more fossil fuel energy is required to produce a metric ton of ethanol than is contained in the ethanol. Michael Wang at Argonne National Laboratory claimed in 2005 that improved agricultural practice had turned this around, so that 35% more energy is produced than consumed.²³ Shapouri maintains that the ethanol contributes 24%

more energy than is required to produce it.²⁴ A consortium in 2004 suggested a figure as high as 67%. The relevant parameter is the EROEI (the energy returned on energy invested). A consensus was thought to have emerged around a figure of 1.3 for corn-based ethanol, while sugar-cane ethanol registered an EROEI of 8.

Even this consensus was disputed by Timothy Searchinger and Joseph Fargione, who claim that changes in land use had not been taken into account. There is almost three times as much carbon in plants and soil as there is in the air. So when the soil is disturbed – when rain forests are cut to plant sugar cane, or prairie is plowed to plant corn, or tropical peat lands are drained to plant palm trees – it releases carbon from the existing plants and the soil into the air.^{25,26} The U.S. Agriculture Department says that for 2008 farmers may convert seven million acres from conservation land to corn. Fargione says that conversion racks up a carbon debt that will take about 90 years to repay.

Obviously each contender makes different assumptions, which it is not our intention to evaluate here. However, there is no question but that expensive corn-based ethanol must be government subsidized if it is to be used in gasoline. If the fuel oxygen mandate is continued, then the government is mandating a subsidized product. This does not make much sense.

16.6.5.3 Biomass as Feedstock

The above controversy seems unlikely to be resolved, and policy is likely to be influenced by political rather than scientific considerations. Meanwhile, various breakthroughs could make the issue clearer. The central one is the use of biomass as feedstock. It is estimated that biomass (which includes residues of the forest industry, corn cobs, oat hulls, and various plants) could supply annually $5\text{--}10 \times 10^{15}$ Btu ($\sim 5000\text{--}10,000$ terajoules or 125–250 million metric tons oil equivalent) of fuel and chemicals by the year 2020. This would amount to 5.7–11.4% of present U.S. energy consumption and other, even more optimistic, estimates set the figure at 25%. The problem is that conventional enzymes cannot break down cellulose, lignin, and so on into its constituent sugars at a reasonable speed. The development of better enzymes is a key research topic.²⁷ Novozymes, the world's largest manufacturer of industrial enzymes, claims to have developed an enzyme cocktail that will turn agricultural wastes into glucose. Poet, a biofuels company currently making wheat bioethanol, claims to have a cellulose-to-glucose facility operating in 2010 and expects to have cellulosic bioethanol by 2012.²⁸ DuPont, after acquiring a biomaterials company Danisco, has announced a 95 million liter/year plant due in 2014.²⁹ More than twenty other companies, including DSM and BASF in Europe, have declared their intention to build cellulosic fuel plants.³⁰ Other feedstocks have been suggested such as municipal solid wastes³¹ and wood,³² and new technologies such as the use of ionic liquids to extract lignins.³³

16.6.5.4 Catalytic Bioforming

A sophisticated system, known as Catalytic Bioforming®, is being developed by Virent Energy Systems and Shell. A 10,000 gallon/year (38,000 liters) pilot plant came on stream in March 2010.³⁴

Cellulosic biomass of almost any kind is first fractionated into cellulose/hemicellulose and lignin, the latter generally being burned to power the refinery. The cellulose/hemicellulose is hydrolyzed with acid (it could be done with enzymes) and gives a mixture of water-soluble C5 and C6 sugars. Depending on the balance of products required, these are subject either to hydrogenation to polyhydric alcohols or hydrogenolysis to give short chain aliphatic compounds, such as glycerol, propylene glycol, and ethylene glycol.

The product stream is subjected to the novel APR (aqueous phase reforming) process in which it is reacted with water over a proprietary heterogeneous catalyst (platinum–rhenium on carbon) at 460–575 K and 1–90 bar to give carbon dioxide, alcohols, ketones, aldehydes, and smaller amounts of alkanes, organic acids, and furans plus hydrogen, which is recycled to the hydrotreating stage. The effluent is heated to 648 K and passed successively over two acid catalysts, tungstated zirconia and zeolite ZSM-5, and high yields of gasoline-range hydrocarbons emerge. These separate naturally from the aqueous stream; hence distillation is not required.

If jet fuel hydrocarbons are required, the alcohols, ketones, and aldehydes are condensed over a multifunctional base catalyst that promotes formation of β -hydroxylactones and β -hydroxyaldehydes, and subsequent hydrogenation and condensation steps give longer chain alkanes.

This is an impressive achievement. Energy consumption is low and the biogasoline has a higher energy content than ethanol. In 2008 it was claimed that it could compete with gasoline if the oil price was above \$60/bbl. On the downside, there are the inevitable problems of gathering and processing solid feedstocks, and the emission of carbon dioxide, dictated by the process stoichiometry. No matter what the process, there is no way round these problems.

16.6.5.5 *Biotechnology Versus Synthesis Gas*

The pretreatment of even the most homogeneous of the above feedstocks is expensive, and the cost of the enzymes is currently on the order of \$150 per metric ton of ethanol compared with the \$33 required to make the process remotely feasible. Genetic engineering could possibly produce better cellulases and hemicellulases and reduce the need for pretreatment through lignin modification. Methods of increasing plant polysaccharide content and overall biomass are also being sought, as is a method of separating ethanol that does not involve distillation. For example, a membrane that would transmit ethanol but not water could be used in a cross-flow system provided it had high enough transmission. A continuous rather than a batch fermentation process would be valuable, and work has also been done on this. Depending on the production method, the EROEI of cellulosic ethanol could be anything between 2 and 32.

The problems with biotechnology are that enzymes operate slowly and give rise to large quantities of waste water. There have been suggestions that biofuels from cellulotics could most cheaply be achieved by brutally abandoning biotechnology, burning the cellulotics to give synthesis gas, and converting that to methanol and then gasoline (Sections 12.5.2 and 12.5.2.4).

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CHAPTER 17

How Polymers Are Made

The polymer industry stands out above all others as a consumer of heavy organic chemicals, and it converts these to the products called plastics, fibers, elastomers, adhesives, and surface coatings. The general terms polymer and resin are used synonymously in the chemical industry, but the terms plastics, elastomers, and fibers have specific meanings, and it is incorrect to refer to all synthetic polymers as plastics. A plastic is a material that is formed or fabricated from a polymer, usually by causing it to flow under pressure. Thus if a polymer is molded, extruded, cast, machined, or foamed to a particular shape, which may include both supported and unsupported film, the polymer can be described as a plastic. Often a plastic contains pigments and additives such as antioxidants, plasticizers, and stabilizers. Fibers and elastomers are defined in Section 17.6.

This chapter includes some of the chemistry of individual polymer manufacture but is intended more as a broad description of how to synthesize a polymer, how to influence its properties, and how these properties relate to end uses that affect everyone's daily life.

In 2008 the U.S. polymer industry produced on the order of 58 million metric tons of polymers.¹ Figure 17.1 shows the pattern based on the published statistics. The large unallocated section may be that part of the production for which an end use is not clearly defined, or it may represent smaller products for which statistics are not reported in detail. Meanwhile, it is clear that the polymer industry is overwhelmingly a manufacturer of plastics – they make up 84% of the allocated tonnages. The fiber and surface coatings sectors shrank between 2000 and 2009, the fibers dropping by a half and the surface coatings by a third.

The approximately 58 million metric tons of polymers can be compared with 290 million metric tons of chemical products produced by the organic chemicals sector. The latter figure refers to chemicals actually isolated before being subjected to another reaction. Thus we might conclude that the polymer industry consumes only about one-fifth of the chemical industry output. Such a conclusion ignores an important element of double counting implicit in the statistics. If one million metric

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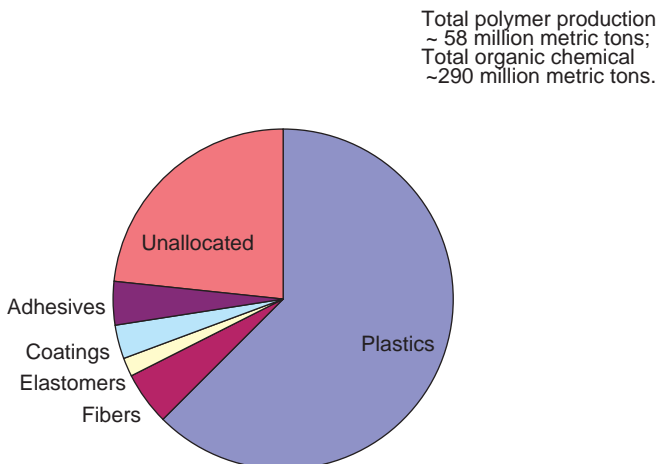


FIGURE 17.1 The U.S. polymer production 2008.

tons of ethylene and three million metric tons of benzene are produced from naphtha and react together to give about four million metric tons of ethylbenzene, which is then dehydrogenated to a like amount of styrene, which in turn is polymerized to almost four million metric tons of polystyrene, then the production statistics will add them all up and record 16 million metric tons of chemicals.

It is difficult to eliminate this element of double counting altogether, but one estimate that we quoted in the second edition was that the 40 million metric tons of polymers produced at the time consumed about 100 million metric tons of chemicals – about 48% of the total of all chemicals produced. Looked at more closely, this figure looks less reasonable. Only about 5% of ethylene goes into ethylene glycol antifreeze (see Fig. 5.3) and it has no other large nonpolymer outlets. Five-eighths of propylene goes into polypropylene and, of the remaining three-eighths, acrylonitrile goes into polymers, as do a substantial fraction of the other products (see Fig. 6.2). C_4 compounds (apart from MTBE which is declining) go into elastomers. Benzene goes into polystyrene, cumene, and cyclohexane, the last two largely finishing in bisphenol A and nylon. While it is possible that the above statistic includes refinery products and fuel uses, we suggest that, if these are excluded, something like 90% of organic chemicals find their way into polymers.

Polymers may be subdivided into two categories, thermoplastic and thermosetting. Thermoplastics soften or melt when heated and will dissolve in suitable solvents. They consist of long chain molecules often without any branching (e.g., high density polyethylene). Even if there is branching (e.g., low density polyethylene) the polymer may still be two dimensional. Thermoplastics may be used in the five main applications of polymers – plastics, fibers, elastomers, coatings, and adhesives – as shown in Table 17.1. These are discussed further in Section 17.6.

Thermosets decompose on pyrolysis and are infusible and insoluble. They have elaborately crosslinked three-dimensional structures and are used for plastics,

TABLE 17.1 Major Applications of Polymers**Plastics**

Extruded products

Low density and linear low density polyethylene
 Poly(vinyl chloride)
 Polystyrene and styrene copolymers (e.g. styrene acrylonitrile)
 High density polyethylene
 Poly(ethylene terephthalate)
 Polypropylene
 Acrylonitrile–butadiene–styrene copolymers
 Cellulose acetate
 Cellulose acetate butyrate

Molded products

Polystyrene and styrene copolymers
 High density polyethylene
 Polypropylene
 Low density and linear low density polyethylene
 Poly(vinyl chloride)
 Phenolics
 Polyacetals
 Urea–formaldehyde
 Melamine–formaldehyde
 Acrylics
 Cellulose acetate
 Cellulose acetate butyrate

Film and sheet

Low density and linear low density polyethylene
 Poly(vinyl chloride)
 Regenerated cellulose (cellophane)
 Acrylics
 Poly(ethylene terephthalate)
 Polypropylene
 High density polyethylene
 Nylon

Foams

Polyurethane
 Polystyrene
 Many others

Fibers

Poly(ethylene terephthalate)
 Nylon (polyamides)
 Aramids
 Polyacrylonitrile copolymers
 Polypropylene
 Rayon
 Cellulose acetate
 Glass

(continued)

TABLE 17.1 (*Continued*)**Elastomers**

Styrene–butadiene rubber
 Polyisoprene
 Ethylene–propylene terpolymers
 Polybutadiene
 Butadiene–acrylonitrile copolymers
 Silicone
 Sulfochlorinated polyethylene
 Styrene–butadiene–styrene thermoplastic rubber

Coatings

Paper and textile applications
 Low density polyethylene
 Polystyrene and styrene copolymers
 Poly(vinyl chloride)
 Poly(vinyl acetate) and copolymers especially with acrylics
 Urea–formaldehyde
 Melamine–formaldehyde
 Conventional coatings
 Alkyds
 Oils
 Acrylics
 Poly(vinyl acetate)
 Poly(vinyl chloride)
 Epoxy
 Cellulose acetate
 Cellulose acetate butyrate
 Urea–formaldehyde
 Urethanes
 Polystyrene and styrene copolymers
 Unsaturated polyesters

Adhesives

Laminating
 Phenol–formaldehyde
 Urea–formaldehyde
 Melamine–formaldehyde
 Conventional
 Phenol–formaldehyde
 Urea–formaldehyde
 Melamine–formaldehyde
 Poly(vinyl acetate)
 Epoxy
 Cyanoacrylate

elastomers (lightly crosslinked), coatings, and adhesives but not fibers. Fibers require unbranched linear molecules that can be suitably oriented by stretching during the spinning as well as drawing processes that get the polymer molecules close together to achieve high tensile strength.

TABLE 17.2 United States Polymer Production 2008

Polymer	Thousand tons	
	2000	2008
Thermosets		
Epoxy resins	314	264
Urea and melamine	1438	1269
Phenolic	1975	1920
Thermoplastics		
ABS	662	514
Nylon (polyamide)	581	521
LDPE	3436	3177
LLDPE	3471	5470
HDPE	6291	7370
Total PE	13198	16016
Polypropylene	7139	7606
Polystyrene	2993	2368
Polyvinyl chloride	6551	5801
Styrene based latexes	686	514
Thermoplastic polyesters	3188	3701
Other engineering plastics	1362	1148
	38724	40496
Fibers		
Cellulosics	161	25
Nylon	1268	760
Polyester	1812	1120
Other synthetic	1433	685
	4675	2590
	44761	46005

Table 17.2 shows the sales of polymers for plastics applications in the United States in 2000 and 2008. If we add together low, linear low, and high density polyethylenes, then polyethylene emerges as the most important plastic worldwide.

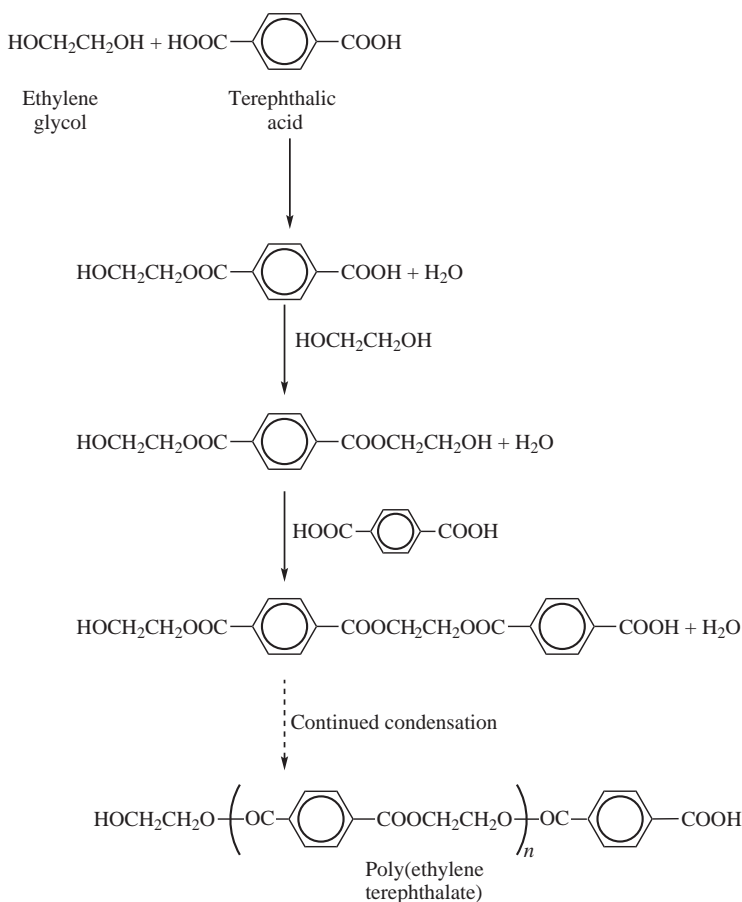
Sales of thermoplastics for plastics applications are almost an order of magnitude greater than those of thermosets in spite of the fact that thermosets, especially urea-formaldehyde and phenol-formaldehyde resins, have been produced commercially for much longer than any of the thermoplastics. The thermosets have been unable to share more extensively in the phenomenal growth of plastics because they are difficult to process and do not lend themselves to the high production speeds that can be achieved, for example, by modern injection molding machines.

17.1 POLYMERIZATION

Before considering polymer properties, we shall describe how molecules link together to form polymers. There are two types of polymerization: addition or chain growth

(also called simply chain) polymerization and condensation or step growth (also called simply step) polymerization. The terms chain and step are more accurate than the older terms, addition and condensation. Chain growth polymerization often involves monomers containing a carbon–carbon double bond, although cyclic ethers such as ethylene and propylene oxides and aldehydes such as formaldehyde polymerize in this way. Chain growth polymerization is characterized by the fact that the intermediates in the process – free radicals, ions, or metal complexes – are transient and cannot be isolated.

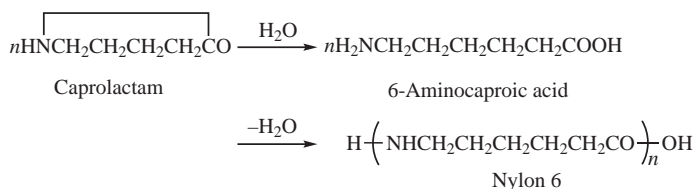
Step growth polymerization occurs because of reactions between molecules containing functional groups, for example, the reaction between a glycol and a dibasic acid to give a polyester.



The low molecular weight intermediates are called oligomers, a term also used for the low molecular weight products obtained by chain growth polymerization. In the polyesterification shown here, an oligomer can have two terminal hydroxyl groups, two terminal carboxyls, or one of each. The hydroxyls can react further with

terephthalic acid and the carboxyls further with ethylene glycol. Alternatively, two oligomers can condense. The continuation of these reactions, familiar from simple esterification chemistry, leads to the final polymer. The step growth or condensation reactions can be stopped at any time, and low molecular weight polyesters (terminated by hydroxyl or carboxyl groups) isolated. Step growth polymerization, as opposed to chain growth polymerization, is therefore defined as a polymerization in which the intermediates can be isolated.

Usually a small molecule such as water is given off, but this is not always so. In the polymerization of the cyclic monomer caprolactam, for example, both functional groups are in the same molecule, and there is no by-product. Indeed, a mole of water is needed to start the polymerization by hydrolyzing the caprolactam to 6-aminocaproic acid. Each molecule of the latter that self-condenses does indeed give off a molecule of water, but it is needed to hydrolyze more caprolactam to 6-aminocaproic acid. Because no small molecule is given off, the reaction reaches an equilibrium in which about 10% of the caprolactam remains unreacted. The monomer and oligomers (see below) that are always present must be removed by washing with water. This polymerization is carried out under the same conditions that are used to produce nylon from two bifunctional reagents and is clearly a step growth reaction.



Caprolactam can also be polymerized by a chain mechanism using ionic initiators. Figure 17.2 demonstrates the ionic polymerization of caprolactam with sodium

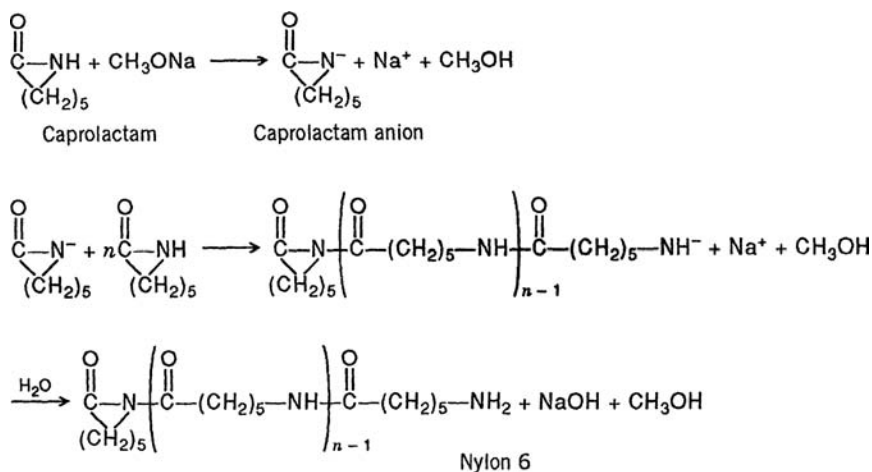


FIGURE 17.2 Ionic polymerization of caprolactam.

Functionality is a measure of the number of linkages one monomer may form with another. A monomer that, when polymerized, may join with two other monomers is termed bifunctional. If it may join with three or more molecules, it is tri- or polyfunctional. Glycols and dibasic acids are clearly bifunctional. Similarly, 6-aminocaproic acid, the reaction product of water and caprolactam, is bifunctional because it contains a carboxyl and an amino group. The functionality rules state that if bifunctional molecules react, only a linear polymer will result (Fig. 17.3a). If a trifunctional monomer (Y in Fig. 17.3b) is added, chain branching can occur. If there is sufficient of it, an elaborate three-dimensional network can result. If some of the chains attached to the Y groups in Figure 17.3c are thought of as coming off at right angles to the plane of the paper, some concept of the three-dimensional structure can be gained. A crosslinked polymer of this kind is essentially one huge molecule.

Glycerol has a functionality of three and, if condensed with a dibasic acid, can give the multifunctional oligomers shown below. Crosslinked polymers soon become insoluble and infusible as their molecular weights increase. The crosslinking may lead to excellent strength characteristics, but the infusibility and insolubility means that such polymers are difficult to convert into shapes. The chemistry of thermoset polymers produced by step growth polymerization is further discussed in Section 17.4.

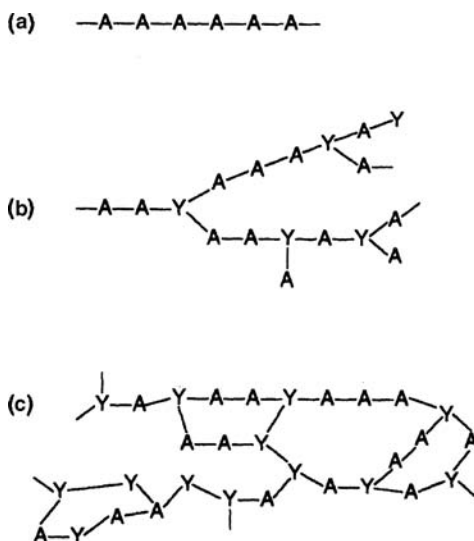
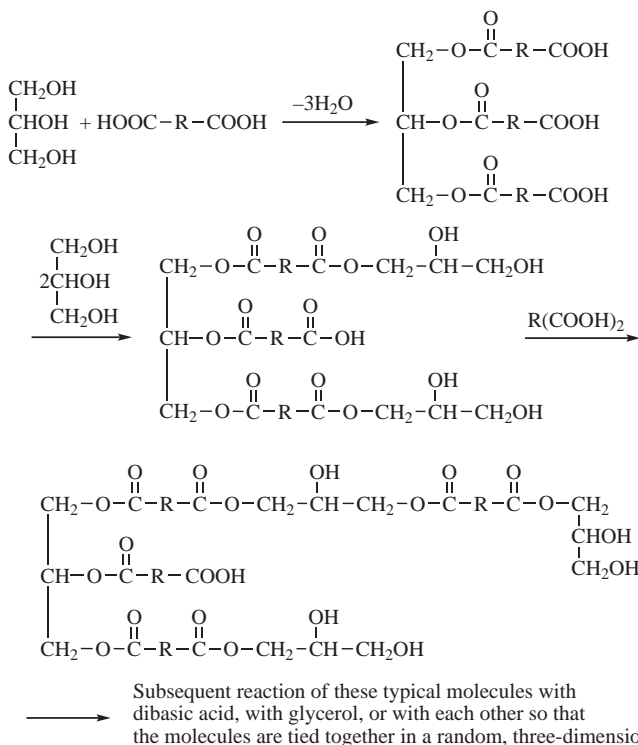


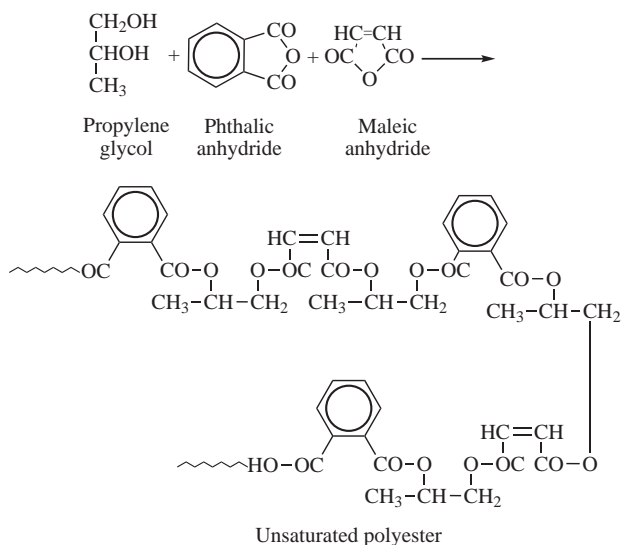
FIGURE 17.3 Linear, branched, and crosslinked structures.



The ethylenic double bond so important in chain growth polymerization has a functionality of two even though the organic chemist would regard the double bond as a single functional entity. However, the ability of the extra electron pair of the ethylenic linkage to enter into the formation of two bonds makes it bifunctional. Thus ethylene polymerizes to form a linear thermoplastic polymer. The double bond in propylene contributes a functionality of two, but propylene also possesses allylic hydrogens that are activated by peroxide initiators so that a crosslinked structure results. Thus propylene has a functionality greater than two toward peroxide catalysts. On the other hand, Ziegler–Natta catalysts do not activate the allylic hydrogens. Propylene shows a functionality of two toward them, and a linear polymer results. This chemistry is harnessed in some ethylene–propylene rubbers. A linear ethylene–propylene copolymer is made with a Ziegler–Natta catalyst. It may then be crosslinked with a peroxide catalyst (Section 5.2.5).

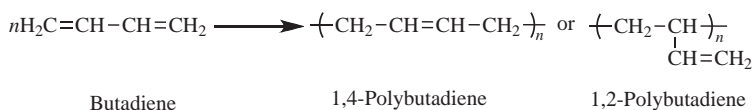
In the production of unsaturated polyester resins, a linear liquid oligomer is made by step growth polymerization, typically of propylene glycol with phthalic and maleic anhydrides. Each of these reagents exhibits functionalities of two in an esterification reaction. The maleic anhydride, however, has a double bond that can undergo chain growth polymerization. Thus subsequent treatment of the unsaturated polyester with styrene and a peroxide catalyst leads to a solid, infusible thermoset copolymer in which polyester chains are crosslinked by polystyrene chains. The maleic anhydride

has a functionality of two in both the step growth and chain growth polymerizations. In chain growth polymerization, crosslinking results because the unsaturated polyester with its multiple double bonds has a functionality much greater than two.



The fact that monomers exhibit different functionalities toward different reagents and polymerization techniques provides a means by which an initial polymerization can give a linear polymer that can subsequently be crosslinked by a different technique. Further examples of this are given in Section 17.4.

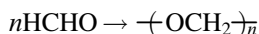
Structures, such as those in butadiene, whose double bonds are conjugated, are considered to have a functionality of only two. When they polymerize, linear polymers are formed that still contain double bonds.



These can subsequently react to form a crosslinked polymer but, in the initial polymerization, butadiene is bifunctional.

Pyromellitic dianhydride has a functionality of two when reacted with diamines, and linear polyimides result as shown in Figure 17.4. On the other hand, this anhydride reacts with water to form a tetracarboxylic acid that has a functionality of four when reacted with compounds containing hydroxyl groups.

The functionality of a molecule is not always obvious. The situation with a double bond has already been discussed. Formaldehyde has a functionality of two and will polymerize to the common laboratory reagent, paraformaldehyde:



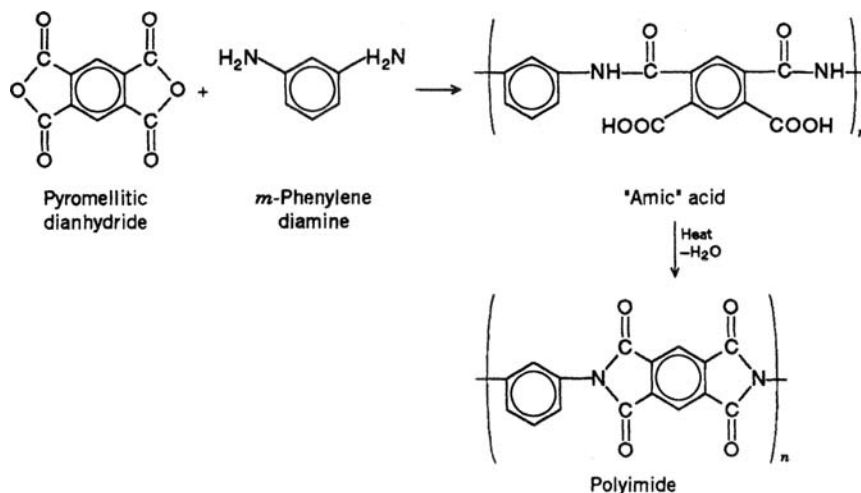


FIGURE 17.4 Polyimide synthesis.

Although very high molecular weights can be obtained, the product is of little commercial value because it “unzips” easily to regenerate formaldehyde. This can be prevented and practical polymers obtained by acetylation of the hydroxyl end groups. Alternatively, a formaldehyde–ethylene glycol copolymer is made and is then subjected to conditions that would normally degrade it. The formaldehyde groups at the end of the chains “peel off” until an ethylene glycol unit is encountered. Depolymerization ceases, and a stable polymer molecule with hydroxyethyl end groups is left with the following structure:



Formaldehyde polymers are known as polyacetals. Aldehydes in general can be polymerized anionically or cationically (Section 17.3.6) to give polymers with a $\sim\text{C--O--C--O--C--O}\sim$ backbone.

17.3 STEP GROWTH AND CHAIN GROWTH POLYMERIZATIONS

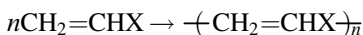
Step growth polymerization can be described as a simple chemical reaction carried out repeatedly. Polyesterification, for example, is brought about by the same catalysts as esterification reactions, and the equilibrium is pushed to the ester side of the equation by removal of the by-product water either by simple distillation or as an azeotrope. A major difference between a simple condensation reaction and a polycondensation is that the high molecular weight of the polymer product increases the viscosity of the reaction mixture if the polymer is soluble in it; if not,

it precipitates. To solve the viscosity problem, the reaction may be carried out in a solvent, a technique that is particularly useful if the polymer is to be used in a surface coating that requires solvent. More often the engineer is called on to devise equipment with powerful stirrers that can accommodate viscous masses.

In the production of many thermoset polymers, polymerization is interrupted at an early stage before crosslinking starts. The product is still fusible and soluble and is known as a “B-stage” polymer. In the B-stage, the polymer can be molded or otherwise treated to put it into the final form such as a film or a part. It can then be totally cured or crosslinked. In situ curing, usually with the aid of heat and a catalyst, is relied upon to build up molecular weight and achieve the crosslinked state. Phenolics are often used as tractable B-stage polymers (Section 17.4). In polyimide formation an intermediate chemical species, an “amic” acid, is formed (Fig. 17.4). This is soluble, albeit in very strong solvents such as dimethylformamide. The solution can, however, be laid down as a film and then heated further to evaporate the solvent and achieve polyimide formation. Polyimides are linear as Figure 17.4 indicates but are almost intractable because of their insolubility and rigidity.

The molecular weight and tendency to gel of a polycondensation polymer may be controlled by addition of a monofunctional compound known as a “chain stopper.” In the production of polymeric plasticizers such as poly(ethylene glycol adipate), for example, butanol is used as a chain stopper. Chain stoppers are also important in the production of alkyds (Section 11.1.2).

Chain growth polymerization proceeds rapidly by way of transient intermediates to give the final polymer. We can write an overall equation,



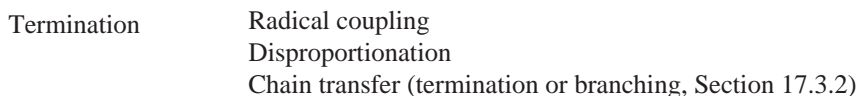
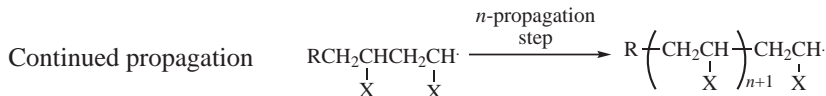
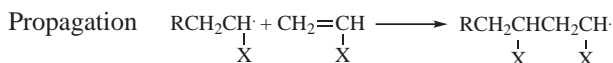
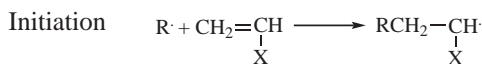
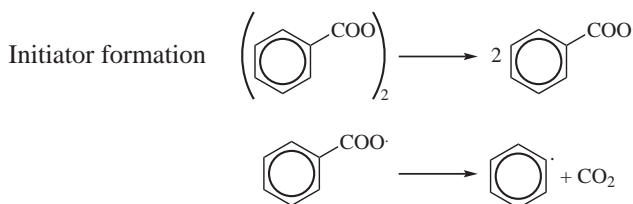
but it provides no indication of the reaction mechanism. Polymerization is started by a chain initiator that converts a molecule of monomer into a free radical or an ion or else by a catalyst that converts the monomer to a metal complex. The free radicals or ions then undergo so-called propagation reactions that build up the polymer chain. In the case of metal complex catalysis, often referred to as Ziegler–Natta catalysis, the propagation takes place on the surface of the metal complex catalyst. Finally, there must be a chain termination step in which the transient intermediate, now a polymer chain, is stabilized.

In chain growth polymerization, repeating units are added one at a time, as opposed to step growth polymerization where oligomers may condense with one another. Propagation and termination steps are very rapid. Once a chain is initiated, monomer units add on to the growing chain quickly, and the molecular weight of that unit builds up in a fraction of a second. Consequently, the monomer concentration decreases steadily throughout the reaction. Prolonged reaction time has little effect on molecular weight but does provide higher yields. At any given time, the reaction mixture contains unchanged reactant and “fully grown” polymer chains but a very low concentration of growing chains. The growing chains cannot readily be separated from the reaction mixture.

In step growth polymerization (Section 17.1) the monomer does not decrease steadily in concentration; rather it disappears early in the reaction because of the ready formation of low molecular weight oligomers. The molecular weight of a given polymer chain increases continually throughout the reaction, and thus long reaction times build up the molecular weight. After the early stages of the reaction, there is neither much reactant nor a great deal of “fully grown” polymer present. Instead, there is a wide distribution of slowly growing oligomers. If desired, this distribution can be calculated and the separate oligomers isolated from the reaction mixture.

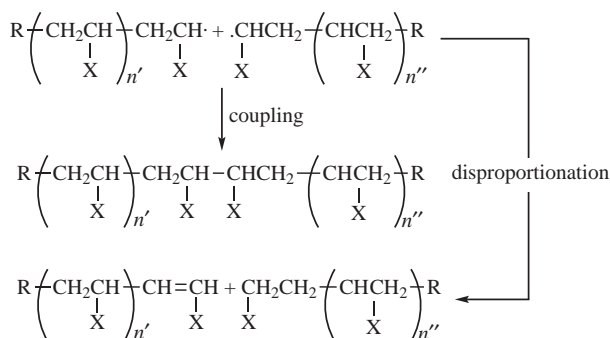
17.3.1 Free Radical Polymerization

Free radical polymerization is initiated by free radicals from compounds such as benzoyl peroxide which, on heating, decomposes to give benzoyloxy radicals, some of which eliminate carbon dioxide to give phenyl radicals. One of the free radicals then adds on to a molecule of monomer such as ethylene, vinyl chloride, or styrene to convert that monomer to a radical. Initiation is now complete, and the initiating free radical is incorporated into one end of a polymer chain. Its concentration in a high molecular weight polymer is so small that it does not affect final properties. The radical now reacts with another molecule of monomer to give a larger free radical, and this chain propagation process continues until the chain is terminated.



The most important free radical initiators are benzoyl peroxide, dicumyl peroxide, dialkyl peroxides (especially methyl ethyl ketone peroxide, used for unsaturated polyester resins, and di-*t*-butyl peroxide), and peroxyesters of the general formula R-CO-O-O-R.

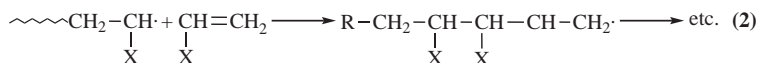
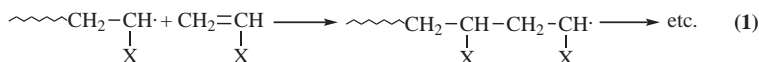
What can stop the chain? The three possible processes are called coupling, disproportionation, and chain transfer. Coupling occurs when two growing free radicals collide head to head to form a single stable molecule with a molecular weight equal to the sum of the individual molecular weights. In the disproportionation reaction, two radicals again meet, but this time a proton transfers from one to the other to give two stable molecules, one saturated and the other with a terminal double bond. Above 60°C polystyrene terminates predominantly by coupling whereas poly(methyl methacrylate) terminates entirely by disproportionation. At lower temperatures both processes occur.



Chain transfer can cause either termination or branching. It is discussed in Section 17.3.2.

Because propagation reactions in chain growth polymerizations are very fast, polymerizations can and sometimes do become explosive. Termination steps occur rarely relative to the propagation reaction, not because they are slow but because the concentrations of free radicals are normally so low that encounters between them are rare.

In the polymerization of ethylene, it makes no difference which end of the molecule is attacked by the free radical. With unsymmetrical monomers such as vinyl chloride or styrene, however, there could be head-to-tail propagation (equation 1), head-to-head propagation, or completely random addition. In the head-to-head case, the side chain or heteroatom X would sometimes occur on adjacent carbon atoms (equation 2).



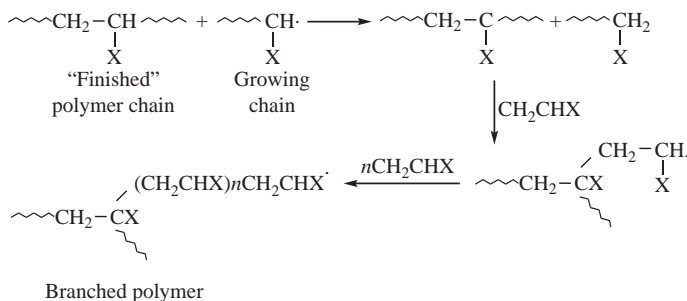
Head-to-head propagation rarely occurs because the unpaired electron in the free radical prefers to locate itself on the $-\text{CHX}$ end of the monomer molecule where it has a better opportunity to delocalize. The free radical is thus more stable. Head-to-tail polymerization is the norm, and only an occasional monomer molecule slips in the “wrong way.” Termination by coupling, of course, creates a head-to-head structure.

The relative rates of the initiation, propagation, and termination processes are reflected in the key property of molecular weight on which many of the other properties of the polymer depend. If the rate of initiation is high, for example, then the concentration of free radicals at any given moment will be high, and they will stand a good chance of colliding and coupling or disproportionating. A high initiation rate will therefore lead to a low molecular weight polymer.

For a high molecular weight polymer, a low initiation rate is required together with a high propagation rate. We might also say a low termination rate, but, because termination steps have no activation energy, they occur on every collision and are diffusion-controlled. The termination rate is decreased by increase in viscosity or decrease of concentration in a system. If propagation and termination steps have comparable rates, a polymer will not result. A propagation rate thousands of times the termination rate is required, and the molecular weight is in fact a function of the ratio of propagation to termination rates.

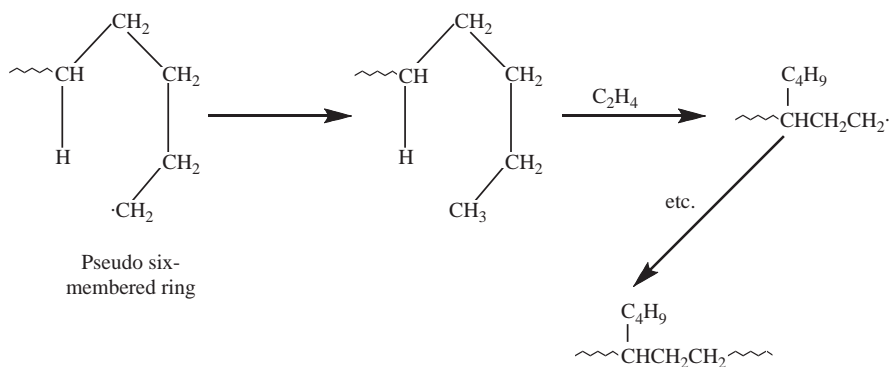
17.3.2 Chain Transfer

Another factor that affects molecular weight is chain transfer. A growing polymer radical may extract a hydrogen atom from a finished polymer chain. This “finished” polymer chain now becomes a radical and starts to grow again. If the hydrogen atom is extracted from the end of the chain, the new chain simply continues to grow linearly. But if, as is more probable statistically, the hydrogen atom is extracted from the body of the chain, then further propagation occurs at right angles to the original polymer chain and a branch forms.



Branching can have a marked effect on polymer properties. It can keep polymer molecules from achieving molecular nearness to each other and hence reduce cohesive forces between them. Correspondingly, branching makes it harder for

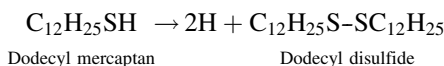
polymer crystals to form (Section 17.5.1). The following equation shows how branching takes place in polyethylene.



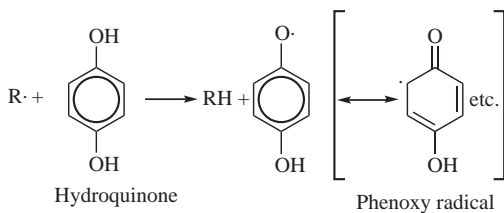
A growing polymer molecule with a free radical end can bend to form a pseudo six-membered ring that facilitates the transfer of the free radical site from the end of the chain to a carbon atom within the chain. The chain then starts to grow from this new site with the net result that the branch has four carbon atoms. Low density polyethylene is indeed characterized by C_4 branches.

Chain transfer can occur not only to another polymer chain but also to a molecule of monomer. The new radical will then propagate in the usual way. If this happens often, a low molecular weight polymer will form.

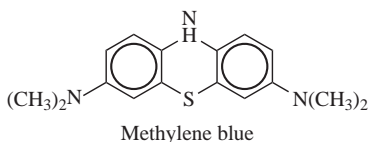
Chain transfer is undesirable except when it is used intentionally to limit molecular weight. It can be controlled by addition of chain transfer agents. These are materials from which hydrogen atoms can readily be abstracted. If a growing radical is liable to extract a hydrogen atom, it will do so preferentially from the chain transfer agent rather than from another polymer molecule. The problem of branching will thus be avoided but not that of reduced molecular weight. Dodecyl mercaptan is used as a chain transfer agent in low density polyethylene and rubber polymerizations. When it loses a hydrogen atom, a stable disulfide forms. The formation of a stable compound after loss of a proton is a key characteristic of a chain transfer agent.



Phenols may be used similarly because they give up their phenolic hydrogen readily and the resulting phenoxy radical is relatively stable and does not add to monomer.



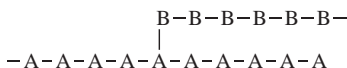
During storage, monomers are sometimes stabilized with polyhydric phenols or related materials (e.g., hydroquinone) and *t*-butylcatechol or aromatic amines (e.g., methylene blue) so that they do not polymerize spontaneously.



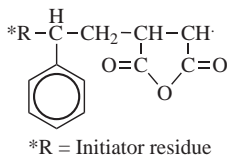
Hydroquinone is ineffective in the absence of oxygen, so its mode of action is probably more complicated than suggested here. If a free radical should appear in the monomer, it immediately accepts a proton from the inhibitor and is “squelched.” To polymerize the monomer, the inhibitor must be removed, usually by distillation.

17.3.3 Copolymerization

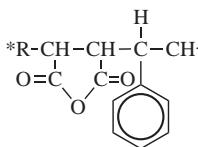
Discussion of propagation rates leads to the topic of copolymerization. Copolymers are made from two or more monomers and are of four kinds – regular, random, block, and graft. In regular copolymers the monomer units alternate in the chain (–A–B–A–B–A–B–A–B–); in random copolymers they follow each other indiscriminately (–A–A–B–A–B–B–A–B–). Block copolymers (Section 17.3.8) consist of a group of one polymerized monomer followed by a group of the other (–A–A–A–A–B–B–B–B–), and graft copolymers result when a polymer chain of one monomer is grafted on to an existing polymer backbone (Section 17.3.9):



Occasionally, a step growth copolymer is regular. An example is based on maleic anhydride and styrene. Maleic anhydride will not homopolymerize but reacts rapidly in a polymerization reaction with another monomer. Thus one styrene monomer will react with a maleic anhydride monomer. The resulting free radical,

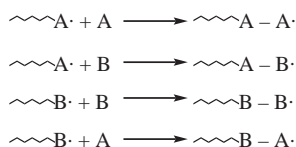


has a choice of reacting further with another styrene molecule or with another maleic anhydride. It chooses the styrene because the maleic anhydride will not react with itself. The free radical,



chooses a maleic anhydride monomer because the reaction rate between styrene and maleic anhydride is much greater than between styrene–styrene. In this way a completely regular copolymer, $\sim\text{S}-\text{MA}-\text{S}-\text{MA}-\text{S}\sim$, is obtained.

In the random copolymer, the monomer units are not in an orderly sequence. To form a random copolymer, the two monomers must react with themselves at a rate comparable to that at which they react with each other. If the propagation rates differ widely, the first polymer molecules to be formed will consist almost entirely of the fast reacting monomer and, when all of it is used up, the slow reacting material will polymerize to give a polymer consisting almost entirely of the slow reacting material. The possible propagation reactions are as follows. It is the relative rates of these processes that decide whether a random copolymer, two homopolymers, or something in between is obtained.



Copolymerization serves several functions. First, a copolymerizing monomer may be included to plasticize the polymer, that is, to make it softer. Because vinyl acetate gives too brittle a film for water-borne paints, it may be copolymerized with 2-ethylhexyl acrylate. Second, the copolymerizing monomer may insert functional groups. In unsaturated polyesters (Section 11.1.3) the maleic anhydride provides double bonds that may subsequently be crosslinked by chain growth polymerization. In elastomers, a comonomer with two double bonds is almost always used. One double bond engages in chain growth polymerization, and the other remains intact on each recurring unit so that sites for “vulcanization” or crosslinking with sulfur are present. Thus butyl rubber is a copolymer of isobutene with a small amount of isoprene.

Finally, copolymerization can be used to reduce crystallinity (Section 17.5.1). Low density polyethylene is about 50% crystalline. By making a copolymer with propylene, this crystallinity is destroyed, and a polymer results that becomes an elastomer on crosslinking.

Copolymerization plays an important role in the synthesis of linear low density polyethylene (LLDPE). High density polyethylene (HDPE) (Section 5.1.3) requires mild conditions for manufacture whereas low density polyethylene (LDPE) requires severe conditions such as 1200 bar and 200°C. Chemists learned how to make a polymer whose properties approximate those of LDPE simply by making a copolymer of HDPE, under the mild conditions HDPE requires, using the comonomers 1-butene, 1-hexene, or 1-octene in concentrations of 6–8% (Section 5.1.4). These destroy some of the crystallinity of HDPE, which is above 90%, lowering it to about 50%, which is the crystallinity of LDPE. LLDPE has greater tensile strength than LDPE because its branches (cf. Fig. 17.3b) are all the same length—two carbons if 1-butene is used, four carbons if 1-hexene is used, and six-carbons if 1-octene is used. Because of its lesser energy requirements, LLDPE production has grown rapidly, although this economic

advantage is partially offset because the C_6 and C_8 comonomers are more expensive than ethylene.

17.3.4 Molecular Weight

We have referred several times to the molecular weight of a polymer. This is not as simple a concept as it sounds. Since the chains in a sample of polymer do not all have the same number of recurring units, the molecular weight of a polymer is always an average. A broad molecular weight distribution is often desirable, for oligomers may serve as lubricants during processing and as plasticizers thereafter.

Molecular weight of polymers is commonly expressed in two ways: by number average M_n and by weight average M_w . The number average is obtained by adding the molecular weights of all the molecules and dividing by the number of molecules. If we have n_1 molecules of molecular weight M_1 , n_2 of molecular weight M_2 , and n_x of molecular weight M_x , then

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \cdots + n_x M_x + \cdots}{n_1 + n_2 + \cdots + n_x \cdots}$$

The weight average, on the other hand, is calculated according to the weight of all the molecules at each molecular weight. Let w_1 be the weight of molecules of molecular weight M_1 , w_2 the weight of molecules of molecular weight M_2 , and so on, then

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + \cdots + w_x M_x + \cdots}{w_1 + w_2 + w_3 \cdots}$$

But the total weight of all molecules with molecular weight w_1 is $M_1 n_1$, so we can substitute $w_1 = M_1 n_1$, $w_2 = M_2 n_2$, $w_x = M_x n_x$, and so on in the above equation, whence

$$\bar{M}_w = \frac{w_1 M_1^2 + w_2 M_2^2 + \cdots + w_x M_x^2 + \cdots}{n_1 M_1 + n_2 M_2 + \cdots + n_x M_x + \cdots}$$

M_n tells us where most of the polymer molecules are relative to the molecular weight distribution. M_w , on the other hand, tells us where most of the weight is regardless of the molecular weight distribution. Because M_w is biased toward molecules with higher molecular weight, it will be larger than M_n .

As an example, consider three persons, two weighing 50 kg and one weighing 100 kg. Their number average weight is $(50 + 50 + 100)/3 = 66\frac{2}{3}$ kg, but their weight average is $(50^2 + 50^2 + 100^2)/(50 + 50 + 100) = 75$ kg. In the first instance, we can consider that a person was selected at random; in the second, that a kilogram of weight was selected at random. The second selection (weight average) will naturally lead to a higher result because the pound of weight will tend to be selected from the heavier persons.

M_w and M_n both provide a narrow view of molecular weight. Their ratio, M_w/M_n , is called the molecular weight distribution and is a measure of the spread. If $M_w/M_n = 1$,

then all the molecules have the same molecular weight, and as the distribution of molecular weights becomes wider this ratio increases.

Boiling point elevation, freezing point depression, osmotic pressure, and end group analysis give number average molecular weight; light scattering and sedimentation methods give weight averages. Viscosity measurements give a value somewhere between the two.

The molecular weight profile of a polymer can be determined only by fractionation. Cumbersome solvent precipitation techniques give numerous fractions, and the molecular weight of each is determined. The fractions must be so narrow that for each of them M_w/M_n is effectively unity.

17.3.5 Polymerization Procedures

Chain growth polymerizations, whether initiated by free radicals as we have already described, or by ions or metal complexes as we describe later, are carried out by four different procedures – bulk, solution, suspension, and emulsion polymerizations.

In bulk polymerization, the monomer and the initiator are combined in a vessel and heated to the proper temperature. This procedure, although the simplest, is not always the best. The polymer that forms may dissolve in the monomer to give a viscous mass, and heat transfer becomes difficult. Heat cannot escape, and the polymer may char or develop voids. If the exotherm gets out of hand, the system may explode.

Even so, the polymerization of ethylene by the high pressure method is a bulk polymerization and is one of the polymerizations carried out on the largest scale. Fortunately, the polymer does not dissolve in the monomer. Instead, it collects in the bottom of the reactor and is drawn off. The exotherm still presents a problem, and the strictest possible control of temperature and heat transfer is necessary to prevent problems. The polymerization of methyl methacrylate to “Lucite” (“Plexiglas,” “Perspex”) is also carried out in bulk.

Fluid bed processes are essentially bulk polymerizations and represent one way of handling the exotherm. They have become popular because they provide an economical way to make standard grades of high density polyethylene, linear low density polyethylene (Section 5.1.4), and polypropylene. The fluid bed comprises small particles of the preformed resin, fluidized by inert gas. The gaseous monomer and catalyst are injected into the fluid bed and the polymer forms around the nuclei provided by the particles of preformed resin. Conversion is only 2% but ethylene is easily recycled.

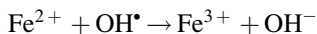
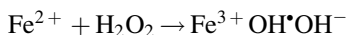
The other polymerization procedures are all designed to solve the problem of heat transfer. In solution polymerization, the reaction is carried out in a solvent that acts as a heat sink and also reduces the viscosity of the reaction mixture. The snags with solution polymerization are first, it is frequently difficult to remove the last traces of solvent from the polymer, and second, this solvent in chain transfer reactions causes low molecular weight polymers to result. Solution polymerization is useful if the product is to be used in solvent. Solvent-based poly(vinyl acetate) adhesive is an example. Slurry polymerization is a variant of solution polymerization and is used for the important polymerizations of ethylene to high density (low pressure) polyethylene in one version of the Phillips process (Section 17.3.11) and for propylene to

polypropylene. A small amount of solvent is combined with the monomer and catalyst in the reactor. The solvent forms a slurry with the catalyst and aids in its distribution throughout the reaction mixture. At the same time it helps to remove exotherm. Initially it was necessary to separate the catalyst by a cumbersome process. This has led to the development of catalysts that separate more readily. Also, catalysts are now available that give such high yields, and thus are present in such low concentrations, that they can be left in the polymer without affecting its properties.

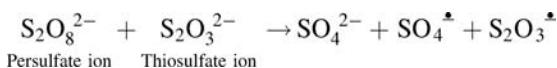
In suspension polymerization, the monomer and catalyst are suspended as droplets in a continuous phase such as water. These droplets have a high surface-to-volume ratio so heat transfer to the water is rapid. The droplets are maintained in suspension by continuous agitation and also, if necessary, by addition of a water-soluble polymer such as methylcellulose that increases viscosity of the water. Finely divided inorganic materials such as clay, talc, aluminum oxide, and magnesium carbonate have a similar stabilizing effect on the suspension. The need to remove these materials is one of the disadvantages associated with their use. Poly(vinyl chloride) is frequently made by suspension polymerization.

The final procedure is emulsion polymerization, a technique that was developed as part of the synthetic rubber program during World War II. The products are particularly useful for the formulation of water-based paints. As its name implies, it uses an emulsifying agent, usually various kinds of soap. In solution these form micelles in which the nonpolar hydrophobic ends of the soap molecules point inward, and the polar hydrophilic groups point outward and interact with the water. If monomer is added, it is absorbed into the micelle to give a stable emulsion particle. If more monomer is added than can be absorbed in the micelles, a separate monomer droplet phase may form that is also stabilized by the soap molecules, the droplets being a micrometer more in diameter.

A water-soluble composite initiator called a "redox" catalyst is then added. This consists of a mixture of a reducing agent and an oxidizing agent. An example is ferrous ammonium sulfate and hydrogen peroxide. In the absence of monomer, the former would reduce the latter in a two-stage process:



If monomer is present, however, the hydroxyl free radical can initiate polymerization. Other redox systems include benzoyl peroxide–ferrous ammonium sulfate, hydrogen peroxide–dodecyl mercaptan, and potassium persulfate–potassium thiosulfate, which gives radical ions:



These polymerizations must be carried out with rigorous exclusion of oxygen, which is an inhibitor for these reactions, even though it is an initiator for low density polyethylene production.

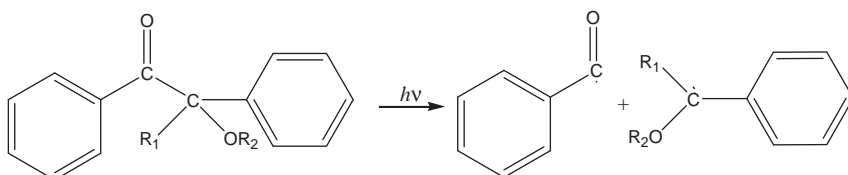
The free radicals diffuse into the micelles, and polymerization takes place within them. Diffusion into the droplets also occurs but, since they have a far lower surface-to-volume ratio than the micelles, virtually none of the polymerization takes place within them. As polymer is formed, the micelles grow by diffusion of monomer from the droplets into the micelles. Rather than providing a site for polymerization, the droplets serve as reservoirs for monomer that will later react in the micelles.

Polymerization within a micelle may take as long as 10 seconds. Very high molecular weights are produced, higher than by any of the three other procedures. The product is a latex, a dispersion of solid particles in water, which is frequently a desirable form for a polymer. For example, poly(vinyl acetate) or polyacrylate latices are used as such for "emulsion" paints. On the other hand, if solid polymer is required, the dispersion must be broken and the polymer precipitated.

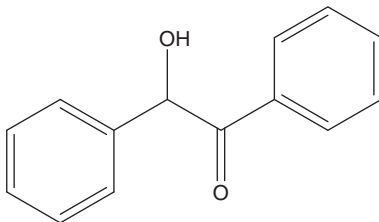
There are two important differences between emulsion and suspension polymerization. In emulsion polymerization the catalyst or initiator is in the aqueous phase, not dissolved in the monomer. Also, particles produced are at least an order of magnitude smaller than those obtained from suspension polymerization.

17.3.5.1 Photoinitiation

A more specialized polymerization procedure is photoinitiation.² This is applied to thin films of polymers such as surface coatings or to the building up of thin layers of polymer in dental repair work. The optimum thickness of layer is limited to about 1 mm. The polymer formulation contains a photoinitiator that absorbs UV or visible light and produces free radicals in a free-radical polymerized system or, less often, cations in a cationic system. There are two classes of photoinitiators. Type I are cleaved by light to give free radicals directly. Benzoin derivatives are the most widely used photoinitiators for polymerization of vinyl monomers:

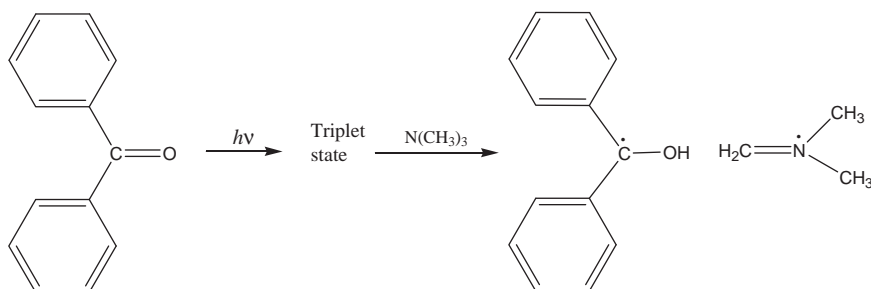


R_1 and R_2 = H or alkyl



Benzoin

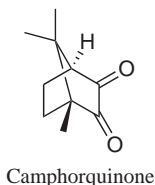
Type II photoinitiators undergo a bimolecular reaction with a coinitiator to give free radicals. Benzophenone and thioxanthone are widely used together with a tertiary amine. The ketone group absorbs radiation to give an excited triplet state, which gives an intermediate excited transfer complex with the amine. Electron transfer gives an amine radical.



Cationic photoinitiators are usually aromatic sulfonium salts such as di(methoxynaphthyl)methylsulfonium hexafluorophosphate or hexafluoroantimonate. Upon photolysis, they produce cations and Brønsted acids.

Type I and type II initiators may be cured by UV light; daylight requires type II or cationic initiators. Daylight-curing formulations are essential for architectural, industrial, and maintenance coatings, where the artifact is too big to be moved. Photopolymerization can be applied generally to cure thin films of unsaturated polyester resins, acrylates, epoxy resins, and other crosslinkable film forming polymers used in coatings, graphic arts, and adhesives. Photoinitiators are widely used in printing inks, especially those for flexographic printing, that is, printing on nonrigid surfaces. Typical polymer systems are polyester acrylates, in which the polyester is dimer-acid-based (Section 15.5), epoxy acrylates, and urethane acrylates. The printed layer is exposed to UV light immediately after printing and cures instantly. These inks have the advantage that they can be water-based.

Photocured composites have replaced amalgam in dental restoration. Unlike amalgam, which simply fills a hole, these resins can be made to bond with dentine and enamel, giving a far stronger structure. The composites comprise a polymer, usually bisphenol A–glycidyl methacrylate or urethane dimethacrylate, a filler such as silica, a silane coupling agent, and an initiator package based on camphorquinone.



The replacement of amalgam gives a stronger restoration, avoids toxic mercury, and permits the patient to eat immediately after treatment instead of waiting for the amalgam to harden.

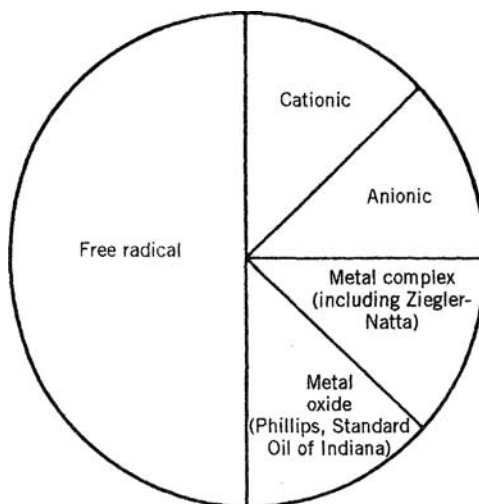


FIGURE 17.5 Methods of polymerization: use distribution (%).

17.3.6 Ionic Polymerization

Free radical initiation is the most widely used way to produce polymers (Fig. 17.5). A second method involves initiation by ions, either anions or cations. Table 17.3 provides a list of ionic initiators useful for polymerization. In Table 17.4 there is a list of monomers and an indication of whether they can be polymerized ionically or cationically. Many of them can be polymerized also by free radicals and by the metal complex catalysts discussed later. Ethylene may be polymerized cationically and also with the aid of free radicals. Propylene, however, has allylic hydrogens on the methyl group, which terminate or transfer the chains terminators (Section 17.3) and any attempt at free radical polymerization leads to low molecular weight crosslinked structures.

As a general rule, monomers containing electron-withdrawing groups are more easily polymerized anionically, whereas those with electron-donating groups are more easily polymerized cationically. Nonetheless, styrene, which contains the electron-withdrawing phenyl group, may be polymerized both anionically and cationically and, for that matter, by free radicals. Cationic polymerization of styrene, however, yields low molecular weight polymers.

Ionic polymerization is usually unsuitable for the preparation of copolymers. This is because the differences in the stabilities of organic ions are much greater than those between the corresponding radicals. It represents a serious limitation to ionic polymerization. An exception is block copolymers (Section 17.3.8), which may be prepared by ionic polymerization because the monomers are added successively not simultaneously.

The initiation step in anionic polymerization is the production of an anion from the monomer by a strong base. This is shown in the equation that follows where butyl lithium is the initiator. Butyl lithium and other anionic initiators such as sodium or potassium amides in liquid ammonia, or sodium cyanide in dimethylformamide, are

TABLE 17.3 Ionic Initiators

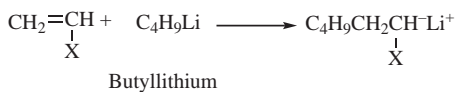
Initiators	Sample Monomers ^a
<i>Cationic Types</i>	
Lewis acids	
BF ₃ (with H ₂ O, ROH, ROR)	1,2
AlCl ₃ , AlBr ₃ (with H ₂ O, ROH, RX)	2,3
SnCl ₄ (with H ₂ O)	3
TiCl ₄	4
FeCl ₃ (with HCl)	3
I ₂ (with Zn halides)	10
Brønsted acids	
H ₂ SO ₄	3 (low mol wt.), 4
KHSO ₄	
HF	3
HClO ₄	
Cl ₃ COOH	5
Active salts	
(C ₆ H ₅) ₃ C ⁺ BF ₄ ⁻ (C ₆ H ₅) ₃ C ⁺ SbCl ₆ ⁻	3
C ₂ H ₅ O ⁺ BF ₄ ⁻	3,4
Ti(OR) ₄	
<i>Anionic Types</i>	
Free metals ^b } in toluene, naphthalene, liquid ammonia, etc.	3,6,7
Na	
K	
Bases and salts	
KNH ₂ , NaNH ₂	3,6
Ar ₂ N ⁻ K ⁺	8
NaCN	
NaOCH ₃	3
RLi, RK, RNa R may be C ₄ H ₉ ⁻ , (C ₆ H ₅) ₃ C ⁻ , C ₆ H ₅ CH ₂ ⁻ , C ₆ H ₅ -CH=CH ₂ ⁻	9

^a 1 = 2-butene; 2 = isobutene; 3 = styrene; 4 = propylene; 5 = isopropenylbenzene; 6 = butadiene; 7 = stilbene; 8 = 2-cyano-1,3-butadiene; 9 = acrylonitrile; 10 = vinyl ethers.

^b Operate by way of production of radical anions and subsequent reaction of these to actual initiating anions.

expensive and not recoverable. Consequently, this procedure is used only where there is no cheaper method of polymerization available and when the value of the product justifies the high initiator cost.

Initiation



Propagation

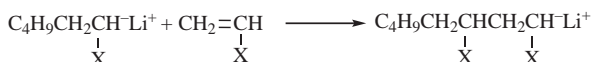
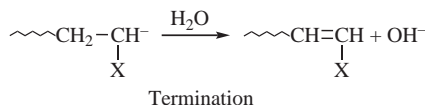


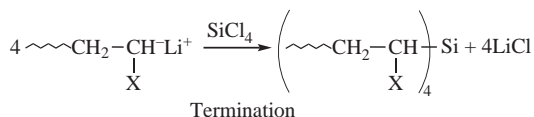
TABLE 17.4 Methods of Polymerizing Monomers

Monomer		Polymerization Mechanism			
		Anionic	Cationic	Free Radical	Metal Oxide or Coordination Catalyst
$\text{CH}_2=\text{CH}_2$	Ethylene		+	+	+
$\text{CH}_2=\text{CHCH}_3$	Propylene		+		+
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	Isobutene		+		
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	Butadiene	+		+	+
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$	Isoprene	+		+	+
$\text{CH}_2=\text{CHC}_6\text{H}_5$	Styrene	+	+	+	+
$\text{CH}_2=\text{CHNO}_2$	Nitroethylene	+			
$\text{CH}_2=\text{CHOR}$	Vinyl ethers		+		+
$\text{CH}_2=\text{CH}-\text{N} \begin{array}{c} \text{CO}-\text{CH}_2 \\ \\ \text{CH}_2-\text{CH}_2 \end{array}$	<i>N</i> -Vinylpyrrolidone		+	+	
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	Methyl methacrylate	+		+	+
$\text{CH}_2=\text{C}(\text{CN})\text{COOCH}_3$	Methyl α -cyanoacrylate	+		+	
$\text{CH}_2=\text{CHCN}$	Acrylonitrile	+		+	



The recombination of a chain with its counterion or the transfer of a hydrogen to give terminal unsaturation, frequent in cationic polymerization (see below), is unlikely in anionic systems. For example, if the counterion is Na^+ the transfer to it of H^- is improbable.

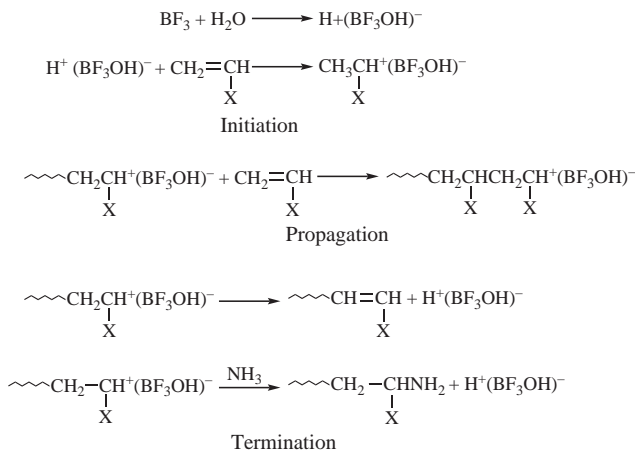
Termination can be brought about by a cation-generating small molecule such as silicon tetrachloride. Four chains can terminate at the silicon atom, so the molecular weight of the polymer has been quadrupled, and it has a “star” shape.



For a “three-armed star-shaped” polymer, a terminating agent such as 1,3,5-tris (chloromethyl) benzene may be used. This is a unique aspect of ionic termination that has no counterpart with free radicals. The radial block polymer is much less viscous than a linear polymer of similar molecular weight, and it is more soluble simply because its shape provides more opportunities for solvation. Thus it couples the benefits of very high molecular weight with easier handling properties. In some respects, it is a halfway stage between linear polymers and the dendritic polymers discussed in Section 17.4.4.

An alternative procedure for preparing star-shaped polymer is to start with multifunctional initiators such as $\text{C}(\text{CH}_2\text{C}_6\text{H}_4\text{Li})_4$. An initiator for a three-armed star-shaped polymer is the alkoxide of triethanolamine, $\text{N}(\text{CH}_2\text{CH}_2\text{ONa})_3$.

Ionic polymerization may also be cationic. Table 17.4 shows which monomers may be polymerized cationically. Initiation is by proton donors such as conventional acids and Lewis acids, and these give rise to carbonium ions. Boron trifluoride in water is typical of a Lewis acid.



The initial step in cationic polymerization catalyzed by aluminum chloride is believed to be



Propagation occurs as in anionic polymerization, and termination occurs when a proton is transferred back to the counterion leaving a polymer molecule with terminal unsaturation. Unlike anionic polymerization, the initiator is regenerated and can go on to generate other chains or even to attack the solvent. Termination can also be brought about by addition of a small molecule such as ammonia, and a polymer with an amine end group is formed. Again the initiator is regenerated.

It is only by way of ionic polymerization that functional end groups can be attached to polymer molecules. With anionic polymer molecules that grow in two directions, as described, CO_2 yields carboxyl groups, whereas ammonia will provide amine end groups; potassium isocyanate, isocyanate end groups; and HCl , chlorine end groups. If the molecular weight of a polymer is very high, the effect of these end groups is negligible. On the other hand, if the ratio of initiator to monomer is such that the number of recurring units is low, an oligomer is obtained. This termination procedure provides an elegant method for the manufacture of bifunctional compounds such as dibasic acids and diisocyanates. But, as so often happens, elegance and expense go together. One mole of expensive initiator is required for every mole of bifunctional compound produced.

17.3.7 Living Polymers

Living polymers are an important ramification of ionic polymerization. The polymer theory that has been outlined so far was developed between 1935 and 1950. The importance of initiation and propagation reactions was recognized, but no one worried very much about termination. It was understood that termination was more difficult in ionic than free radical polymerization because the charges on the growing chains repelled one another, but it was assumed that termination would come about somehow or other.

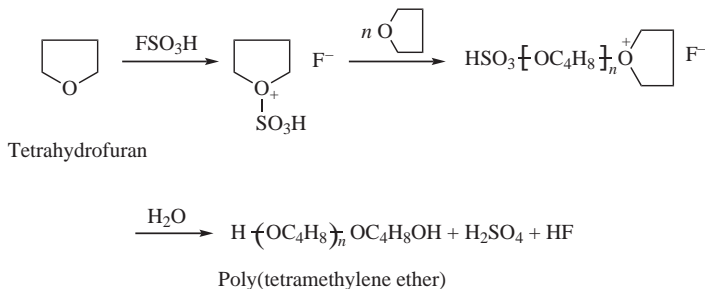
Eventually it was realized that it did not have to occur at all. If styrene is polymerized ionically with sodium naphthalide in tetrahydrofuran solution, and care is taken not to introduce agents that terminate chains, a polymer is formed whose chain length can be estimated from the viscosity of the polystyrene solution. The ends of the chains are unterminated, and the polymer is described as "living." If further styrene is added, weeks or even months later, there will be a marked increase in viscosity showing that the polymer chains have started to grow again once they are supplied with fresh monomer.

17.3.8 Block Copolymers

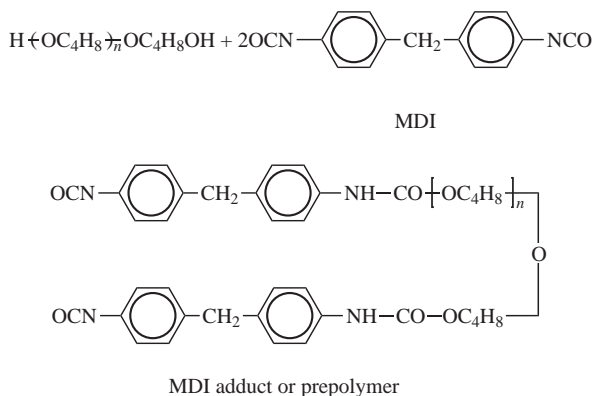
Instead of styrene, in the above example, another monomer such as isoprene may be added to the living polymer, and a copolymer results. Copolymers can be achieved by other means (Section 17.3.3), but they are usually random. With the living polymer

technique, the copolymer is ordered, consisting of a chain of X molecules followed by a chain of Y molecules. If desired a further set of X molecules or of any other monomer can be added. Such materials are called block copolymers.

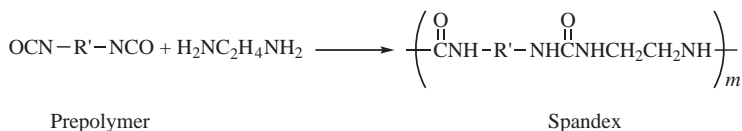
Block copolymers can also be made by condensation techniques. Spandex is an elastomeric fiber whose use over the last three decades has grown at a rapid rate. It comprises a block polymer in which there is a flexible block comprising poly(tetramethylene ether) made by oligomerizing tetrahydrofuran to obtain a hydroxyl-terminated polyether.



Reaction of two moles of the polyether with one of methylene diphenyl diisocyanate (Section 9.3.1) yields an isocyanate-terminated prepolymer. The fluorosulfonic acid, because it presents ecological problems, is being replaced by solid acid catalysts.



The prepolymer, on reaction with ethylene diamine, yields a copolymer with a hard polyurea block adjacent to the soft polyether block. Elasticity is contributed by crimping.



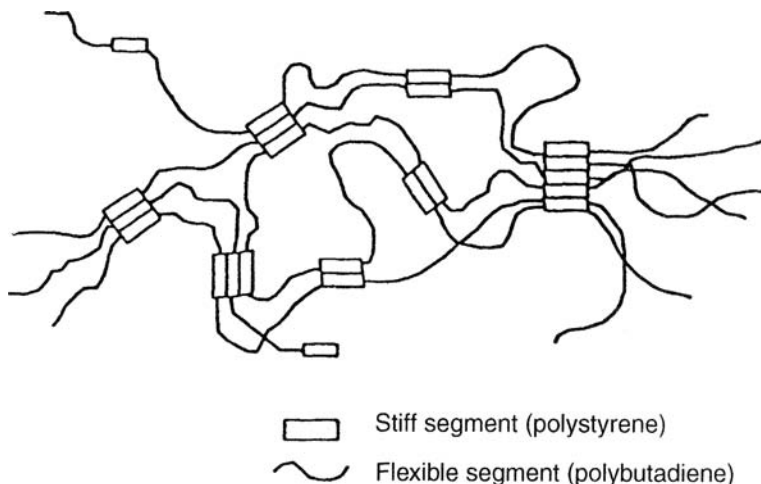


FIGURE 17.6 Block copolymer: styrene–butadiene–styrene.

Condensation reactions can be used to prepare block polymers only if the reactions take place at low temperatures. At high temperatures, existing bonds in many polymers break and reform to provide random distribution and thus a random copolymer.

Block copolymers have industrial applications, especially in the formation of so-called thermoplastic elastomers. The two blocks may be insoluble in one another and thus tend to repel each other. They will, however, tend to associate with similar blocks in other polymer molecules. This is illustrated in Figure 17.6 for a styrene–butadiene–styrene block copolymer. It is quite different from the common free radical polymerized styrene–butadiene rubber, which is a random copolymer. Polybutadiene is a flexible rubbery material; polystyrene is hard and brittle. Furthermore, polystyrene is highly insoluble in polybutadiene. The polystyrene blocks therefore associate with other polystyrene blocks with which they are more compatible, and physical bonding, that is, Van der Waals forces, results. Although these forces are not very strong they nonetheless give an element of crosslinking so that the polymer at room temperature has many of the properties of a crosslinked material. At higher temperatures, however, the weakness of the forces dissociates the “crosslinks” so that the polymer can be processed as if it were a simple thermoplastic.

The useful range of temperature for a block copolymer is determined by the glass transition temperatures (T_g) of the blocks that constitute it. The glass transition temperature is a property of amorphous polymers and is discussed in more detail in Section 17.5.2. At this stage it is sufficient to say that, if an amorphous polymer is melted and then allowed to cool, it will cease to be soft, pliable, and plasticizing at its precise glass transition temperature and become hard, rigid, and glassy.

If the styrene–butadiene–styrene block copolymer (e.g., Shell’s Kraton) is to be an elastomer it must be used above the T_g for polybutadiene. Equally, if it is to retain physical crosslinking it must be used below the T_g for polystyrene. By varying the flexible and rigid blocks other thermoplastic elastomers result, some of which are now articles of commerce. Two are of interest because of their high service temperatures. One is a block copolymer of poly(tetramethylene ether) with hydroxyl end groups, obtained from tetrahydrofuran, and poly(butylene terephthalate) from terephthalic acid and 1,4-butanediol (DuPont’s “Hytrel”). Its service temperature ranges from -50°C to 150°C , appreciably higher than that for the styrene–butadiene–styrene copolymer. The other is a block copolymer of polypropylene as the soft segment with a hard segment comprising fully cured ethylene propylene diene monomer (EPDM) rubber (Section 5.2.5). This is Monsanto’s “Santoprene” and has a service temperature of -50°C to 135°C . High temperature properties are also obtained by Shell in a hydrogenated version of styrene–isoprene–styrene.

Polymers of this sort have found application in rubber footwear, in rubber soles for shoes, as asphalt modifiers, and in both solvent-based and hot melt adhesives.

17.3.9 Graft Copolymers

Chains are usually grafted onto a polymer backbone by creation of a free radical site along the backbone, which initiates growth of a polymer chain. Less often, the backbone possesses functional groups, and chains can be condensed onto it.

An example of graft copolymerization is the production of high impact polystyrene. Polystyrene is a useful low cost plastic. Unfortunately, it is brittle and under stress it tends to craze or stress crack. These defects are alleviated by graft copolymerization, although the grafted polymer is no longer transparent. Polybutadiene is dissolved to the extent of 5–10% in monomeric styrene and an initiator added. Because polybutadiene readily undergoes chain transfer, polystyrene chains grow on the polybutadiene backbone, and an impact-resistant graft copolymer results (Section 7.1.1).

Polyacrylonitrile chains can be grafted onto a starch backbone with the aid of a ceric sulfate initiator or ionizing radiation from a cobalt 60 source. Typically, three chains of acrylonitrile, each with a molecular weight of about 800,000, graft onto each starch molecule. The graft copolymer has markedly different properties from starch itself and is able to absorb as much as 1000 times its own weight of water.

A polymer that has a main chain with two or more three-way branch points and linear side chains, so that there is one long branch per repeat unit, is said to be a comb polymer. If one or more of the branch points has a functionality of four or greater, it is said to be a brush polymer. Brush and comb polymers in general are used to stabilize colloids.³

Graft copolymers have also proved useful in the formulation of a nonstick chewing gum. “Modern” chewing gum was first based on chicle, a natural latex based on the synthetic rubber polyisobutene. It was originally exported from Mexico in the 1860s as a rubber substitute but failed to find a market. Many chewing gums are based on rubber, which is cheaper. Other widely chewed formulations are copolymers of styrene and butadiene or ethylene and vinyl acetate. Sweeteners and flavors are added, and these are removed during chewing, leaving the base polymers, known as cud. The cud is discarded and, being hydrophobic, sticks to sidewalks, flooring, and other surfaces. In the United States, about 300,000 metric tons of chewing gum is produced each year, and 120,000 metric tons of irresponsibly discarded material enters the environment. The removal of discarded cud, for example, by steam stripping, freezing, or corrosive chemicals is an expensive business. In 2005 the London Underground (Subway) spent \$4 million to clean its stations and trains.

A new gum formulation, known as Revolymer™, consists of an amphiphilic polymer mixed with the base. It comprises a graft copolymer of polyisoprene with ethylene oxide, in which the ethylene oxide is grafted onto the pendant double bonds of the polyisoprene. These poly(ethylene oxide) side chains are hydrophilic and interact strongly with, for example, dodecylbenzene sulfonate. Thus the cud may be washed away by detergents. In the longer term, water can infiltrate into the cud giving access to microorganisms, and within six months the cud breaks down naturally into small particles.⁴ The nonstick gum came onto the market in October 2010.

17.3.10 Metal Complex Catalysts

The third method to bring about chain growth polymerization is by the use of metal complex catalysts. Karl Ziegler, who spent World War II at the Kaiser Wilhelm Institute in Germany trying to find ways to oligomerize small molecules into gasoline, found that titanium tetrachloride or titanium trichloride combined with an alkylaluminum catalyzes the polymerization of ethylene. The two components of the catalyst form a solid complex, a proposed structure for which is shown toward the end of this section. Ziegler found that his catalyst produced a high molecular weight linear crystalline polyethylene without any of the chain branching or oxygen bridges obtained in the high pressure free radical polymerization. It was stronger and denser than the conventional material. The conditions required – about atmospheric pressure and 60°C – were astonishingly mild. Ziegler offered his discovery to ICI in the United Kingdom at a remarkably low price. ICI was heavily committed to its own high pressure process and was not interested. Other companies did license his process throughout the world, but a competing process developed by Phillips Petroleum in the United States proved to have advantages (Section 17.3.11) and initially was more widely used. Thus Ziegler’s contribution, which attracted well-earned attention throughout the scientific world, did not find its greatest application in polyethylene manufacture.

In 1955, about three years after Ziegler's breakthrough, the Italian chemist Giulio Natta, who was working for the Italian chemical giant Montecatini, tried the new catalyst system on propylene. It does not take great scientific intuition to realize that if a catalyst works on ethylene it might also work on propylene. This, however, had not been the case with free radical polymerization. The allylic hydrogens on propylene were labile and easily displaced, so that several free radical sites developed on the monomer and growing polymer. A useless, low molecular weight, crosslinked polymer was obtained. With Ziegler catalysts, however, the propylene polymerized smoothly to a high molecular weight linear polymer, and in addition – and this was the dramatic thing that won Ziegler and Natta a Nobel Prize – the polymer was stereoregular. Few discoveries in organic chemistry have created as much interest or excitement.

Several companies filed patents almost simultaneously on polypropylene production and a bitter 30-year patent fight ensued. Phillips Petroleum Company emerged the victor in the United States with a composition of matter patent on crystalline polypropylene. The inventors, P. Hogan and R. Banks, had tried a supported chromia–silica–alumina catalyst on propylene in an attempt to prepare C_6 and C_8 oligomers in the gasoline range and obtained a mostly liquid polymer with about 10% of a solid material. This solid turned out to be identical with Natta's polypropylene, hence the patent. In further work, it emerged that the catalyst was useless for polypropylene production but worked for ethylene – see below.

A stereoregular polymer may be defined as one in which the substituent groups are oriented regularly in space. Structure (a) of Figure 17.7 shows such a polymer with a substituent, CH_3 , in a regular formation. The carbon atom on which the substituent occurs is asymmetric; that is, four different groups are attached to it. It had long been recognized that polymers could contain asymmetric carbon atoms; indeed, natural rubber was just such a polymer. But Natta was the first person to synthesize such a polymer in which all the asymmetric carbons had the same orientation. This polymer is said to be isotactic because all the substituents are similarly placed. Another type of stereoregularity is shown in Figure 17.7b in which the substituents point alternately forward and backward. Such polymers are said to be syndiotactic. Low temperatures favor formation of syndiotactic structures, but they are difficult to synthesize with Ziegler–Natta catalysts. They can more easily be made with metallocenes (Section 17.3.12). The conventional nonstereoregular polymers (Fig. 17.7c) have their substituents placed randomly and are said to be atactic.

The discovery of Ziegler–Natta catalysis meant that almost overnight a procedure had become available for polymerization of unsaturated compounds that could not be polymerized by way of free radicals. The method was versatile and offered scope for further research. There are many transition metal salts besides the titanium trichloride and tetrachloride that Ziegler used and an equally large number of organometallic compounds with which to combine them. The adding of ligands increased the possibilities for influencing results. Since Ziegler's discovery hundreds of combinations and thousands of ratios of constituents have been evaluated. Polymer chemists today have power to achieve practically any

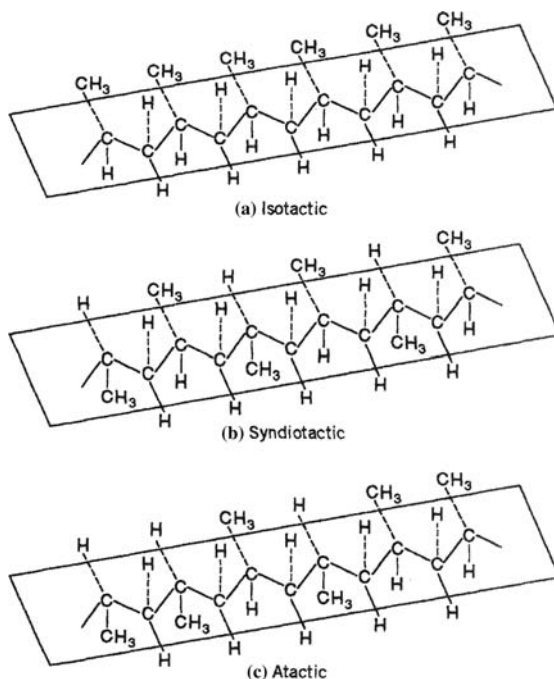


FIGURE 17.7 Stereoregular and atactic polymers.

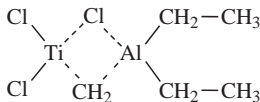
molecular configuration they think will give them the properties they are seeking. It is this versatility that makes Ziegler–Natta catalysis such a powerful tool. Metal oxide catalysis (Section 17.3.11), so important for ethylene polymerization, does not have this versatility.

This is illustrated by the polymerization of butadiene. Polybutadiene may have either a 1,2 or a 1,4 configuration (Fig. 17.8). The 1,4 polymer has a double bond, and the chain structure can be *cis* or *trans*. The 1,2 polymer has vinyl side chains, and these can be arranged in atactic, isotactic, or syndiotactic configurations. Thus five different polybutadienes exist, and all of them have been synthesized with the aid of Ziegler–Natta catalysts.

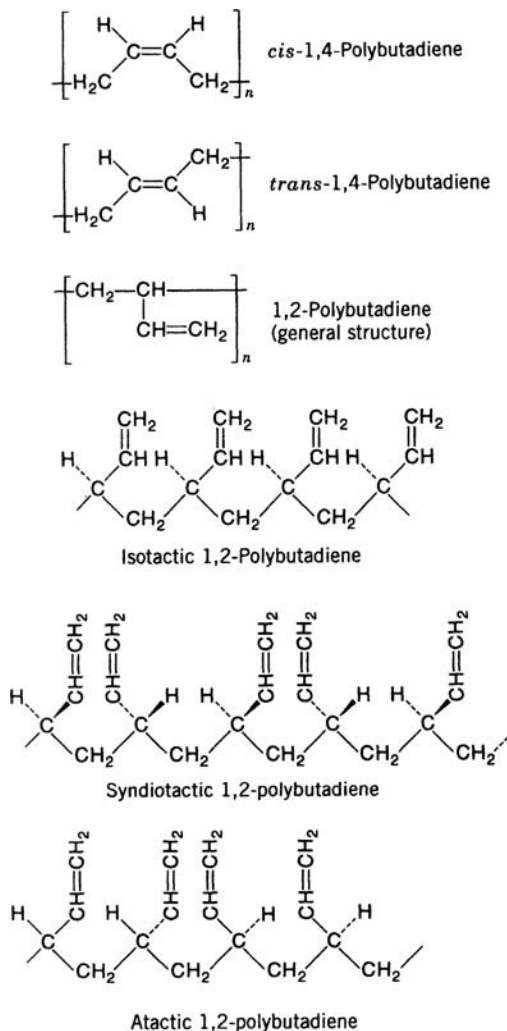
The stereospecificity of Ziegler catalysts has allowed chemists to do what nature can do, with its highly specific enzymes. Nature is able to synthesize optically active compounds, sterically complex antibiotic molecules, and also stereoregular polymers. Natural *hevea* rubber is *cis*-1,4-polyisoprene, while *trans*-1,4-polyisoprene is the nonelastomeric *balata* or *gutta percha*. In the syntheses of hevea rubber in nature, every step is catalyzed by an enzyme. The starting material is acetic acid, a material manipulated with particular ease by nature as is illustrated by its various metabolic pathways in the body. The final step is the polymerization of the monomer, isopentenyl pyrophosphate, which nature prefers over isoprene, by a polymerase present in the rubber plant.



What causes stereospecificity? How do Ziegler–Natta catalysts work? It is known that polymerization takes place at active sites on the catalyst surface. The catalyst is an electron-deficient solid complex of an aluminum alkyl and a titanium halide, the alkyl group on the titanium atom coming from the alkyl aluminum portion of the catalyst. This is one of several possible structures.



The electron deficiency occurs between the titanium–carbon and carbon–aluminum bonds. Titanium has an octahedral configuration with one ligand vacancy, as shown in Figure 17.9a, and a monomer, for example propylene, may become π -bonded to the titanium at the vacancy as in (b). It is then inserted into the chain as in (c) with the

**FIGURE 17.8** The isomeric polybutadienes.

regeneration of the vacant orbital with a different orientation (**d**). Continued addition would lead to a syndiotactic polymer and, to give an isotactic polymer, the chain must migrate back to the original site (**e**). The ligand vacancy again exists, so that the same progression can happen all over again, and another propylene molecule can be incorporated into the alkyl chain. This is the propagation step, and the polymer chain grows by successive insertion of monomer units at the surface of the titanium complex catalyst.

The system is heterogeneous, and the catalyst is insoluble in the monomer and in the solvent. The insertion of monomer molecules takes place at the solid–liquid interface, and the polymer chain grows from the insoluble catalyst into the solvent.

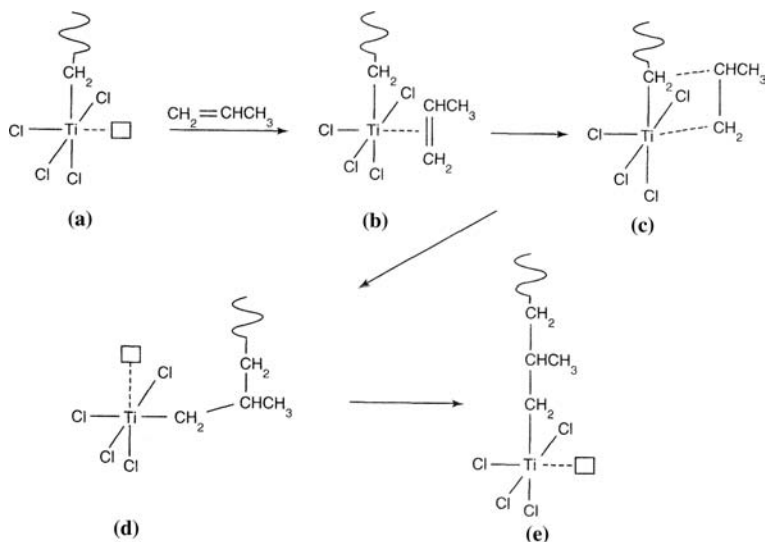


FIGURE 17.9 Mechanism of Ziegler-Natta polymerization.

It is the solvating effect of the solvent on the polymer that attracts the chain away from the catalyst surface and into the solvent and allows further monomer to have access to the titanium atom. Some homogeneous metal-catalyzed polymerizations using ligands can also be carried out.

The mild conditions in the use of Ziegler-Natta catalysis are not only a bonus but also a prerequisite for it. At higher temperatures, bonds around the catalyst would tend to break and reform, and stereospecificity would be lost. The mild conditions also ensure linear polymers and eliminate the branching that is characteristic of free radical initiation. Furthermore, the linear chains can get very near to each other, which gives them high cohesive strength and crystallinity and confers certain desirable properties discussed in Section 17.5.1.

17.3.11 Metal Oxide Catalysts

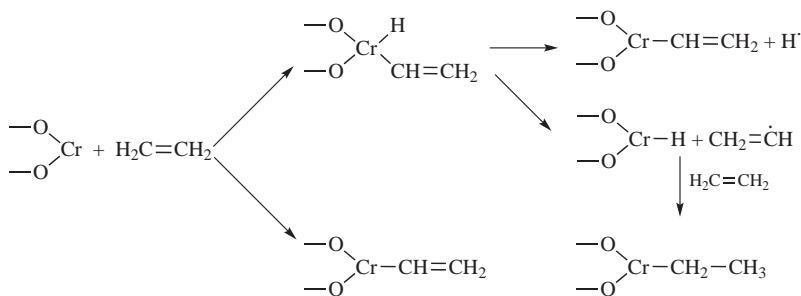
Before Ziegler discovered his catalyst, studies on supported metal oxide catalysts were underway. Researchers for Standard Oil of Indiana developed a molybdenum oxide catalyst supported on silica or alumina that gives high density polyethylene. Their discovery predated Ziegler's, but they did not exploit it because a consultant's evaluation was negative. The consultant, interested in making film, could see no virtue in a stiff, structural-like polymer. The conventional wisdom associated with this story is that it is not enough to invent. One must also recognize the importance of the invention.

Another oxide catalyst system, chromic oxide on silica or alumina, was developed almost concurrently with Ziegler's catalyst by Phillips Petroleum. With it, polymers can be obtained of higher molecular weight than those obtained by the Ziegler

method, and these tend to be intractable. For example, it is difficult to remove them from the kettle. More tractable polymers result when hydrogen and about 1% of a comonomer, 1-butene, are included. The hydrogen controls molecular weight by serving as a chain stopper, which can be regarded as a chain transfer agent (Section 17.3.2). The comonomer controls density. The reaction takes place in a hydrocarbon solvent at 100°C and 40 bar.

Chromic oxide is the most active catalyst, although oxides of Ti, Zr, Ge, and Th are also effective. The best supports are silica or aluminosilicates with low alumina contents. It is important that they have low mechanical strength to permit the breakup of the catalyst particles during polymerization.

X-ray studies suggest that the catalytically active species is Cr(II) and that the polymerization centers contain isolated chromium moieties. Polymerization is initiated by the formation of chromium–carbon bonds on the surface of the catalyst to give a chromium alkyl. The oxidative addition of ethylene to a divalent chromium ion with vacant coordination positions may take place by one of the following mechanisms:



Propagation probably occurs as in Ziegler–Natta catalysis by the sequential insertion of ethylene molecules into the chromium–carbon bond.

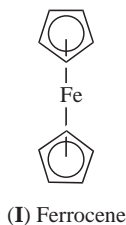
The mechanism of metal oxide catalysis is less well established than that of Ziegler–Natta catalysis. Theoretical interest, perhaps unjustifiably, is less, because, as noted above, neither the Standard Oil of Indiana nor the Phillips process can be used to make polypropylene.

17.3.12 Metallocene and Other Single Site Catalysts

Metallocene-based single site and constrained geometry catalysts are the latest development in the design of “tailored” polymers.⁵ In the 1930s, ethylene was first polymerized industrially to low density polyethylene at high pressures with free radical initiators, then in the 1950s to high density polyethylene at much lower pressures with metal oxide and Ziegler–Natta catalysts. In the 1980s, addition of α -olefin comonomers to Ziegler polyethylene provided linear low density polyethylene at low pressures, which inhibited growth of the high pressure process. It might have seemed as if the possibilities had been exhausted, but technology moves inexorably. In 1991, Exxon opened a plant for production of polyethylenes based

on so-called metallocene single-site catalysts, and Dow opened a plant based on constrained geometry single-site catalysts in 1993. These innovations have caused great excitement.

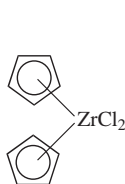
Metallocenes are organometallic coordination compounds in which transition metals are sandwiched between cyclopentadienyl rings. The first metallocene was ferrocene (**I**). Its rings are capable of free rotation and are parallel to one another. Compounds of catalytic interest are discussed below.



The key difference between metallocene catalysts and the conventional Ziegler–Natta catalysts is that Ziegler–Natta catalysts are heterogeneous and have many non-identical active sites, only some of which are stereospecific. Metallocene catalysts, on the other hand, are homogeneous or supported and have a single active polymerization site. As a result, polymers made with them are effectively a single molecular species, having a very narrow molecular weight distribution. Comonomers are taken up in a uniform manner, and their distribution within the polymer chains will be similar. This narrow distribution provides polymers with lower crystallinity, greater clarity, lower heat seal temperatures, and better resistance to extraction. In foodstuffs, extraction of even tiny amounts of low molecular weight polymers adds unpleasant taste and odor. Because metallocene polymers have very low amounts of such low molecular weight materials, they add less taste and odor.

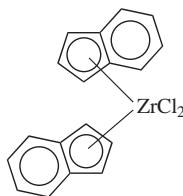
The drawback of the narrow distribution is that ease of processing is diminished. Lower molecular weight polymers act as plasticizers for the processing of the higher molecular weight material. This problem is overcome in three ways. First, addition of conventional Ziegler–Natta catalysts to metallocenes or use of two different metallocene catalysts can give broad or bimodal molecular weight distributions. Second, a controlled amount of long chain branching can be arranged to give narrow molecular weight distribution branched polymers that are more readily processed. Third, low molecular weight polymer, still with a narrow molecular weight distribution, can be added to the formulation.

The metallocenes of catalytic interest are those of the group IVB metals, titanium, zirconium, and hafnium. Structure (**II**) is a typical zirconocene. Metallocene rings are not necessarily parallel and they may be substituted. The cyclopentadienyl ring can be part of a condensed ring system such as fluorene or indene (**III**), and the cyclopentadienyl rings may be joined by silyl or alkylene bridges (**IV**, **V**). Such metallocenes do not allow ring rotation and restrict access to the metal. By definition, metallocenes contain two cyclopentadienyl rings but monocyclopentadienyl compounds of transition metals are sometimes also included in the term.



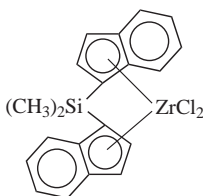
Bicyclopentadienyl zirconium dichloride

(II)



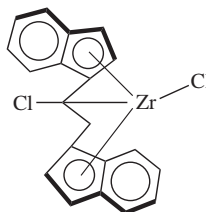
Bi-indenyl zirconium dichloride

(III)



Silyl-bridged zirconocene

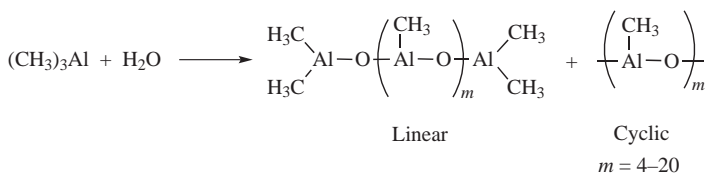
(IV)



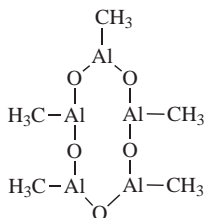
Alkylene-bridged zirconocene

(V)

Metallocene catalysts are of low activity unless used with a cocatalyst, usually a methylaluminoxane but sometimes an ionic activator. Methylaluminoxanes, in turn, are linear or cyclic polymers formed when trimethylaluminum reacts with water:



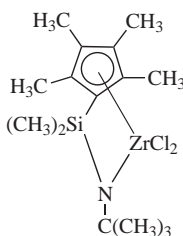
An example of a cyclic methylaluminoxane with five mesomer units is



A simple example of a single-site catalyst suitable for polymerization of ethylene is the reaction product of the zirconocene (II) and a methylaluminoxane. Compound (V) is also used with methylaluminoxane and (II) is used with the ionic activator $\text{C}_6\text{H}_5\text{N}^+ (\text{CH}_3)_2\text{B}^-(\text{C}_6\text{H}_5)_4$. The mechanism of the polymerization process is similar to that of conventional Ziegler-Natta polymerization. The monomer π -bonds to the metal atom and then inserts itself into the growing polymer chain, as was shown in Section 17.3.10. The activity of the metallocenes is high. One gram of a proprietary

metallocene is claimed to generate 4000 pounds of polypropylene, a ratio of 1.8 million to 1.

The most advanced group of metallocene catalysts are the constrained geometry catalysts. These are based on a constrained geometry ligand attached to a transition metal catalyst center. A group IV transition metal is bonded to a cyclopentadiene ring and the ring and a heteroatom are bonded to both by a suitable bridge. An example suitable for ethylene copolymers is



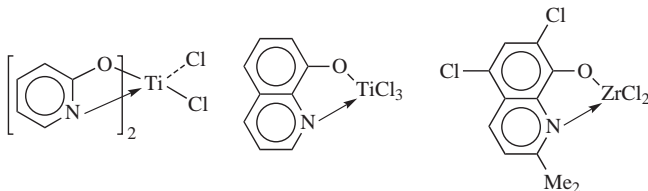
(*tert*-butylamino)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silane-zirconium dichloride

The cyclopentadienyl–zirconium–nitrogen bond angle is said to be less than 115° , and the metal is therefore more open for monomer and comonomer insertion. It permits the use of higher olefins such as octene, vinylcyclohexene, and even styrene as comonomers and also allows polymer molecules with terminal unsaturation to act as comonomers to give long chain branching. The branching permits easier processing, as mentioned above.

The ethylene–styrene copolymers prepared via constrained geometry catalysts are “pseudorandom.” After incorporation of one bulky styrene unit, the active site becomes crowded and at least one unit of ethylene must be added before there is again room for a styrene. Thus the polymer is not iso- or syndiotactic but all the phenyl groups in the polymer are separated by at least two methylene groups. The product is amorphous (unlike conventional Ziegler–Natta polymers) and elastomeric. The ethylene-1-octene polymer is also elastomeric.

17.3.12.1 Single Site Nonmetallocene Catalysts

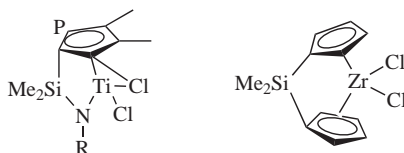
In addition to metallocene-based polyolefin catalysts, other single-site nonmetallocene catalysts have been under development by a number of polyolefin producers. Equistar has introduced nonmetallocene materials based on titanium or zirconium atoms with quinolinol or pyridinol ligands:



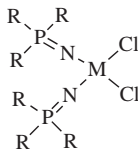
Nova has developed new families of single-site nonmetallocene catalysts based on phosphole and phosphinimine ligands. A wide range of high density and linear low

density polyethylenes can be tailored by use of these high activity catalysts in conjunction with Nova's Advanced Sclairtech reactor technology.

Phosphole catalysis

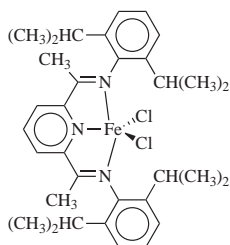


Phosphinimine catalysis

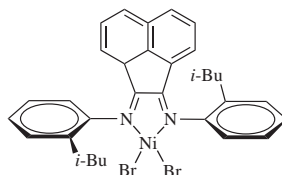
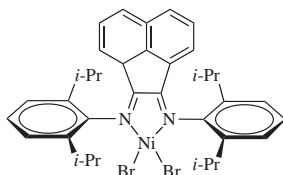
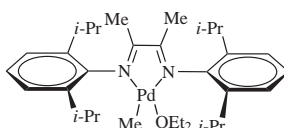
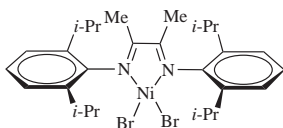


17.3.12.2 Late Transition Metal Catalysts

All the single-site catalysts discussed so far have been based on early transition metals such as titanium and zirconium. In 1996 DuPont, working in collaboration with the University of North Carolina, developed single-site polyolefin catalysts based on the late transition metals, nickel and palladium. This work was subsequently extended to catalysts based on iron and cobalt. Independently, a team composed of personnel from BP and Imperial College, London, has also developed novel iron and cobalt polymerization catalysts. These highly active catalysts have tridentate pyridine and bisimine ligands. The bisimine ligands are bulky substituted arylamines.



Pyridylbisimine complexes



α -Bisimine complexes (*i*-Pr = isopropyl; *t*-Bu = *tert*-butyl)

The bulky substituents are believed to retard the rate of chain transfer and are key to the high molecular weight polymers that can be made using these catalysts. The cobalt compounds generally exhibit an activity that is an order of magnitude lower than the iron analogs. Late transition metal single-site coordination catalysts bring the promise of a range of polymer structures, from the highly branched low density structures afforded by nickel and palladium systems to the highly linear high density products from iron and cobalt catalysts. Perhaps the most exciting property of these late transition metal catalysts is that they are not sensitive to trace amounts of water or other polar compounds, a negative characteristic of classical Ziegler–Natta catalysts. This feature allows these late transition metal catalysts to carry out copolymerizations of ethylene with such polar monomers as methyl acrylate.

17.3.12.3 Commercial Prospects of LLDPEs⁶

Metallocene catalysts got off to a slower start than expected at the beginning of the millennium. Initially Exxon offered a range of ethylene copolymers with propylene, butene, and hexene and Dow offered a range of ethylene-1-octene copolymers. The new catalysts gave polyolefins with unprecedented strength and clarity, but the drawbacks were the expense not only of the catalyst but also of the methylaluminoxane cocatalyst. Furthermore, many resins, notably LLDPE, were harder to process than Ziegler–Natta LLDPE or LDPE because of the narrow molecular weight distribution. Metallocenes were only useful to the best equipped processors. Also, the economic downturn at the beginning of the 2000s did not encourage innovation.

The biggest use initially was for bags for shipping bananas, because the film had high tear resistance. The target markets, where metallocene-based products could sell at a premium, included food packaging, multiply packaging, and heavy duty sacks. The film had improved film sealability, clarity, and toughness. Its use permitted downgauging of film, that is, its production in thinner gauges without loss of strength. In addition, polyethylene blow molding grades were introduced for making small personal care and cosmetic bottles. This grade of resin offers high gloss, comparable to that of polypropylene, plus greater flexibility than glossy HDPEs. Metallocene LLDPE resins are also finding use in the extrusion coating of paperboard. Compared with conventional LDPE, LLDPE, and ethylene-vinyl acetate extrusion coating resins, the metallocene resin has a much higher peel strength. A novel application was the production of a more durable artificial turf based on metallocene medium density polyethylene.

Very low density polyethylenes (Section 5.1.7) are used for hose and tubing, ice and frozen food bags, food packaging and stretch wrap, as well as impact modifiers when blended with other polymers. It is one area where metallocene material is mandatory.

The last decade has seen steady improvement in metallocene catalysts, which give easier processing and cost reductions, particularly of the cocatalyst system. In spite of the slow start, by 2009 five million metric tons of LLDPE was consumed, nearly 25% of the global LLDPE market.

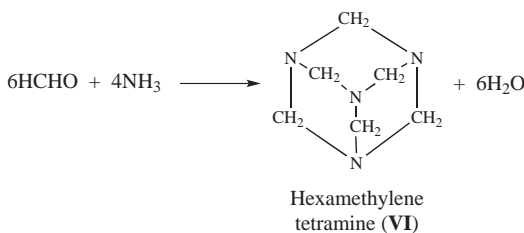
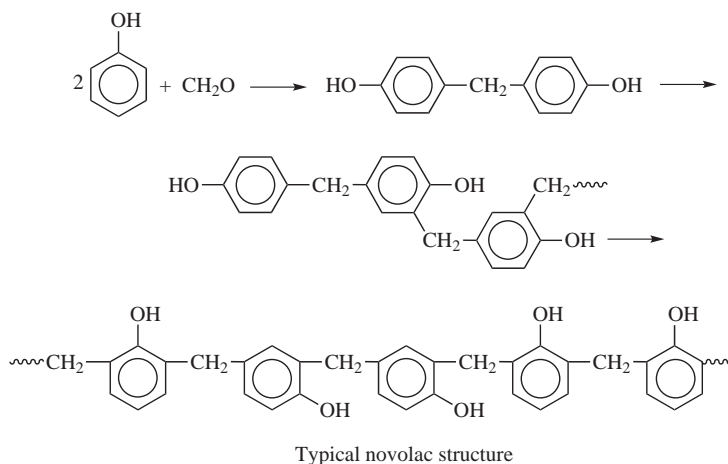
Single-site polypropylene and HDPE are finding very slow market penetration. Metallocene polypropylene was introduced into U.S markets in 1996 and continues to be used only for niche applications. It has been used largely in nonwoven fiber and

specialty injection molding applications. Syndiotactic polypropylene is available in quantity for the first time but, owing to its high cost, is still in market development. Atactic polypropylene for such applications as adhesives and bitumens is planned. About 1.4 million metric tons of metallocene polypropylene was consumed in 2009, which is only 2–3% of the global polypropylene market.

17.4 EXAMPLES OF STEP POLYMERIZATION

17.4.1 Phenoplasts and Aminoplasts

There are two types of phenolic resins (phenoplasts), known as novolacs and resoles. Both are made by step polymerization. Novolacs are made by condensing excess phenol with formaldehyde in the presence of an acid catalyst. Fusible polymers result, with the phenol rings joined by methylene bridges but no free methylol groups. They are linear thermoplastic resins that may be stored or sold in that form. Crosslinking via the formation and condensation of free methylol groups is brought about by heat in the presence of a curing agent that provides more formaldehyde under alkaline conditions. An example is hexamethylenetetramine, a condensate of formaldehyde and ammonia, the latter providing the alkaline conditions. The products are called two-stage resins.

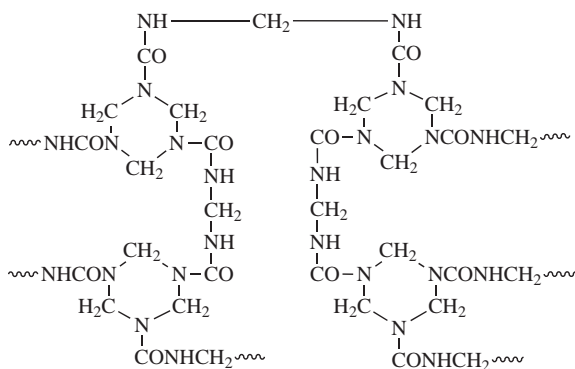


Resoles are made with an alkaline catalyst and sufficient formaldehyde to allow for crosslinking. The initial stage is the production of the simplest methylolphenols,

saligenin and homosaligenin, followed by trimethylolphenols. The methylolphenols condense to give di- and trimethylolphenols and then low molecular weight linear polymers called resoles, which contain occasional oxygen bridges. These are the A-stage resin and are thermoplastic and soluble in organic solvents. If left to go to completion, the process would give a crosslinked structure in one operation (a “one-stage” resin). However, the reaction is stopped at a so-called B-stage before crosslinking occurs. At that stage, the polymer is nearly insoluble but still fusible under heat and pressure. It still contains free methylol groups. The resin has sufficient shelf life for use in compounds for automotive and electrical applications. Crosslinking is brought about by further heating and pressure, which causes the free methylol groups to condense. Typical structures are shown in Figure 17.10.

In these reactions the formaldehyde shows a functionality of two while the phenol has three active sites – two positions *ortho* and one *para* to the hydroxyl group. Only two of them are used in novolac formation, because insufficient formaldehyde is present to react with all three. Thermoplastic phenolics are useful for the preparation of varnishes and result from the condensation of formaldehyde with *p*-substituted phenols.⁷

Urea will also give crosslinked resins with formaldehyde (aminoplasts) under slightly alkaline conditions (Section 12.5.1.3). Methylolureas are formed first. There follows a series of condensations that include ring formation, and the product is a complex thermoset polymer of poorly defined structure of which the following may be typical.



Crosslinked urea–formaldehyde

Urea has a functionality of four in urea–formaldehyde resins, corresponding to the four labile hydrogen atoms. Melamine (Section 12.5.1.3) with three amino groups and six labile hydrogens has a functionality of six, and it too will form thermoset resins with formaldehyde – the so-called melamine–formaldehyde resins.

17.4.2 Polyurethanes

Polyurethanes are polymers consisting of units joined by urethane (carbamate) links --NH--(C=O)--O-- . They result from the reaction of di- or polyisocyanates with diols or

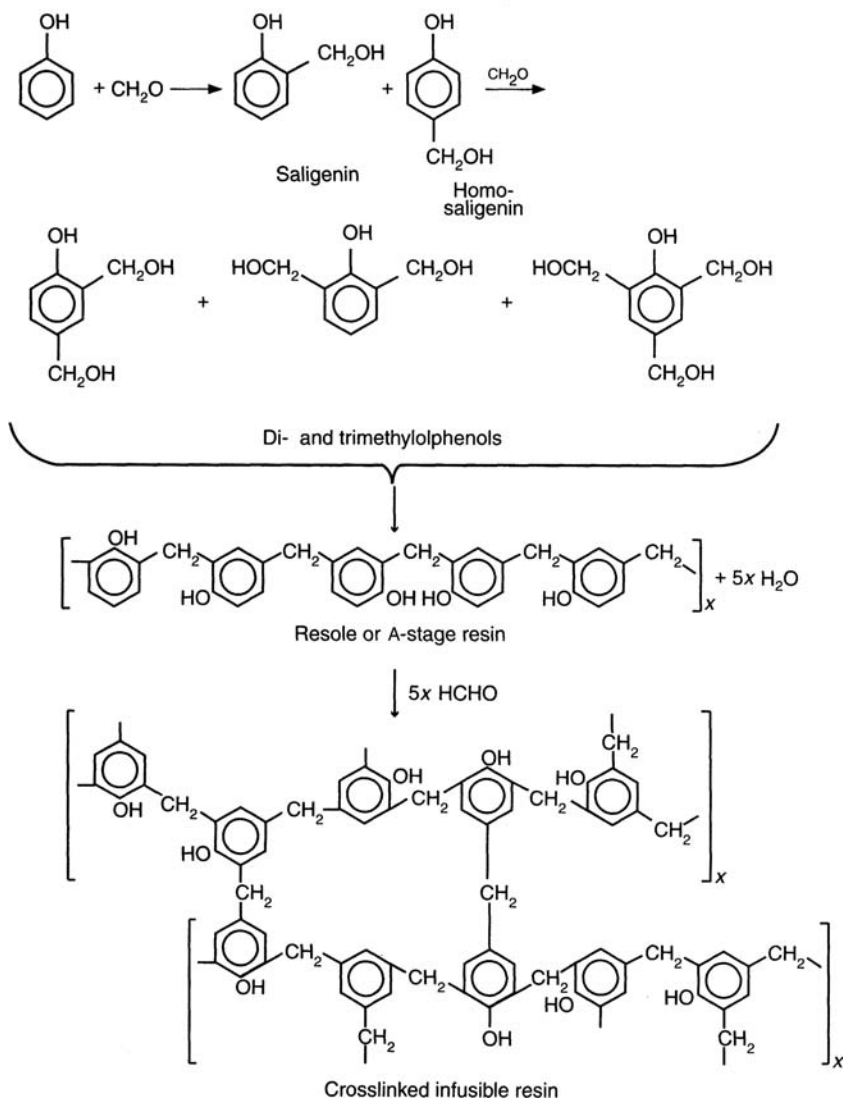
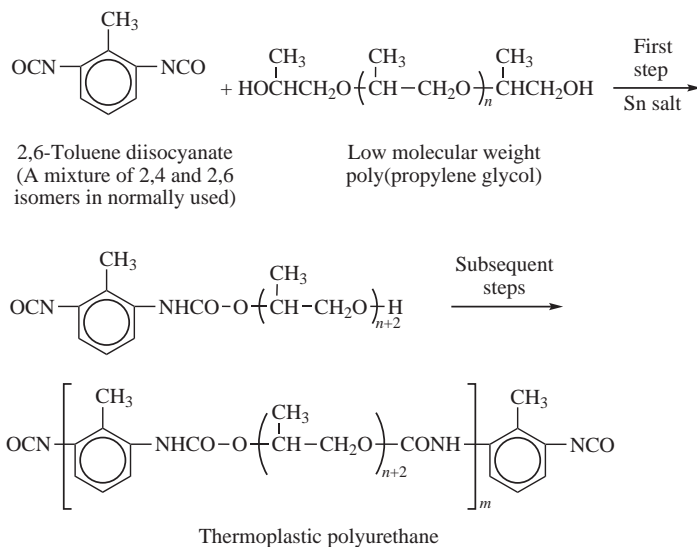


FIGURE 17.10 Formation of resoles and crosslinked phenolic resins.

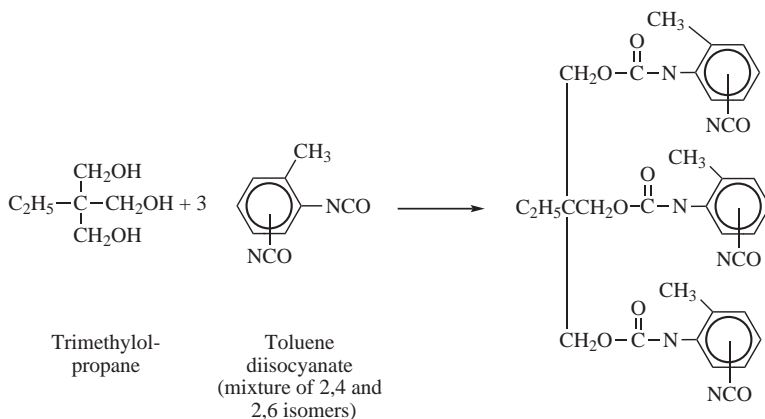
polyols. They can be manufactured by a one-step process in which the main reactants are mixed with catalysts, fillers, reinforcing and coloring agents, blowing agents, and minor constituents and placed in a mold to give the final product. Alternatively, a two-step process is employed in which a relatively high molecular weight prepolymer is assembled first. It is then reacted with a low molecular weight diamine, diol, triamine, or triol to give two- or three-dimensional higher molecular weight

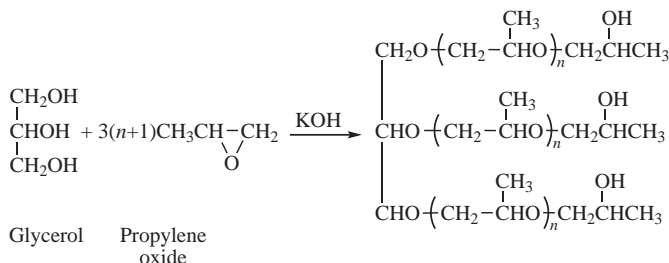
polyurethanes. An example is MDI prepolymer, described in Section 9.3.1. The two-step process is the basis for RIM (reaction injection molding) technology and also avoids the handling of toxic isocyanates during shipment and final processing.

If a diol undergoes step polymerization with a diisocyanate, a linear thermoplastic polyurethane is obtained because both monomers are bifunctional.



Poly(propylene glycol) is a bifunctional oligomer synthesized from propylene oxide (Section 6.8.2). To obtain the more useful crosslinked polyurethanes, trifunctional reagents are required. Sometimes toluene diisocyanate (TDI) is converted to a trifunctional reactant by reaction with trimethylolpropane. The new reagent has the advantage of being considerably less toxic than TDI because of its lower vapor pressure. Alternatively, trifunctional hydroxyl compounds may be made by reaction of propylene oxide with glycerol or trimethylolpropane:

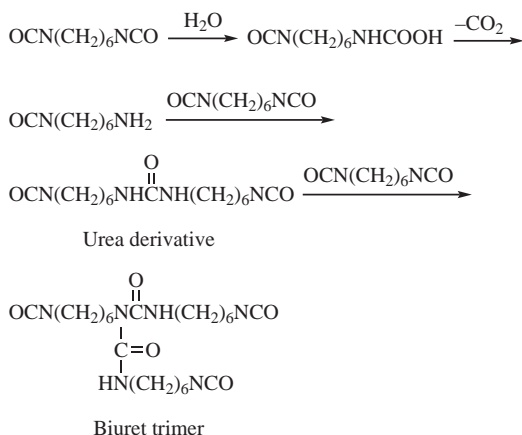




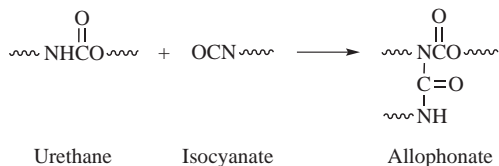
Historically, polyurethane has been made from petrochemical polyols, although castor oil (Section 15.1) is a naturally occurring triglyceride that contains three hydroxyl groups and is a useful starting material. The idea of replacing these polyols with biobased polyols is not new, but the poor performance, color, quality, consistency, and odor of previous biobased polyols have restricted them to limited markets. They also suffered from poor chemical reactivity, resulting in foam with inferior properties.

Cargill, the largest private U.S. company, has recently developed biobased polyols (BiOH™) for several polyurethane applications, including flexible foams, which are technically the most difficult. The carbon-carbon double bonds in soybean oil are converted to epoxide derivatives and then these derivatives are further converted to polyols at mild temperatures and ambient pressure. BiOH polyols are said to provide excellent reactivity and high levels of incorporation leading to high-performing polyurethane foams of higher quality than those based on petrochemicals.

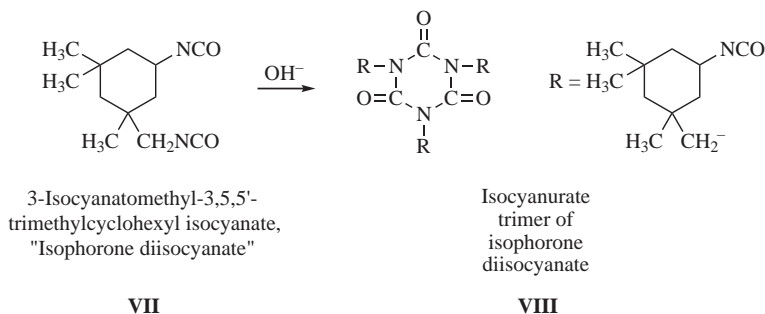
Toluene diisocyanate is the raw material for about 60% of polyurethanes. MDI, which is 4,4'-diphenylmethane diisocyanate and oligomers of it, is second in importance. The presence of the trimer and tetramer in the product mixture means that the product has a functionality greater than two. The aliphatic isocyanate, for example, hexamethylenediisocyanate, HMDI, is toxic and is used in the form of a trimer with a biuret structure. A biuret forms from the interaction of an isocyanate group with a urea. It exemplifies a second type of linkage found in polyurethanes. The HMDI biuret trimer forms as follows:



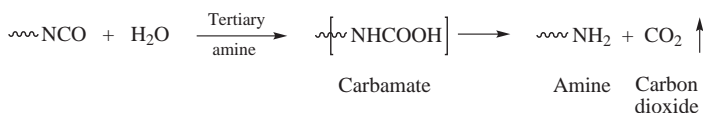
A third linkage, found in polyurethane foams, is the allophanate group, which forms from the interaction of an isocyanate with a urethane linkage.



Still another form in which isocyanates are used is as isocyanurates. These are isocyanate trimers and have an advantage over biurets in being more stable. A typical isocyanurate is the trimer of 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, trivially known as “isophorone diisocyanate” (**VII**). The conversion to trimer (**VIII**) takes place in the presence of a basic catalyst. Isocyanurates have cyclic structures within the foam matrix, giving a harder, more thermally stable structure. Rigid foam products of this kind are used in the construction sector.



In the formation of polyurethane foams, carbon dioxide for foaming may be produced by the addition of water, which gives a carbamate, which in turn decomposes to an amine and CO_2 :



This, however, is an expensive way to obtain a gas for foaming, and specialized foaming agents are used. When water is added, urea linkages form by the condensation of the amine with more isocyanate:



Polyurethane foams contain both these and biuret linkages.

The global polyurethane market in 2007 was about 12 million metric tons, with the United States accounting for about 40% of this. That makes polyurethanes the

largest of the crosslinked thermosetting resins. The properties of a polyurethane are primarily determined by the choice of polyol. Linear difunctional polyether polyols (Section 6.8.2) give soft, elastic, flexible polyurethanes; polyfunctional polyols give more rigid products. The isocyanate has a secondary influence. The rate at which formulations cure depends on the number of functional isocyanate groups and their reactivity. Polyurethanes made with aromatic diisocyanates yellow with exposure to light, whereas those made with aliphatic diisocyanates are stable.

Probably the most widespread use of polyurethanes is as foams. These can be closed cell, in which gases remain trapped in the foam bubbles, and open cell, in which most of the foam cells interconnect. The structure is engineered by addition of surfactants and the time for which curing is allowed, long times tending toward open cells. In general, closed cell foams are rigid and open cell foams are flexible. The blowing agents were originally chlorofluorocarbons, but since the Montreal Treaty (see Table 12.2), they have been replaced by agents such as carbon dioxide, pentane, 1,1,1,2-tetrafluoroethane (HFC-134a), and 1,1,1,3,3-pentafluoropropane (HFC-245fa). Chlorinated blowing agents are said to remain in use in many developing countries.

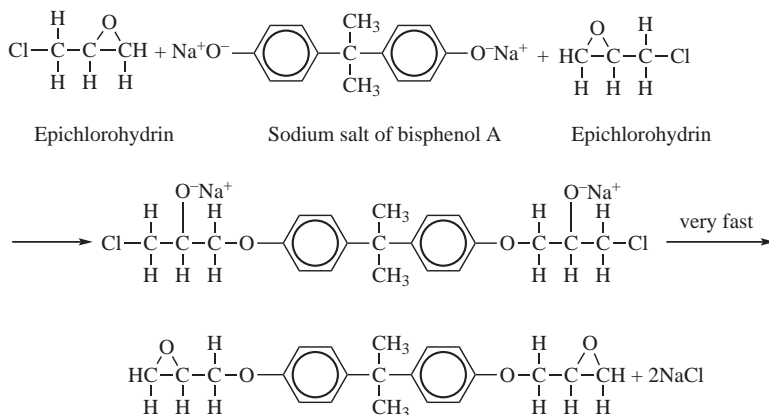
Flexible foams are used in bedding, upholstery, vehicle seats, and carpet underlay. Rigid foams are used for thermal insulation panels. The closed cell structure not only makes the foam better for building purposes, but also prevents gas diffusion, thus enhancing the insulating properties. Soft solid (nonfoamed) elastomeric polyurethanes are used for gel pads and print rollers, while low density elastomers (foamed) are used in footwear. Hard, solid polyurethanes are used for electrical potting compounds and in electronic instruments. Spandex is a partly polyurethane block copolymer and was discussed in Section 17.3.8.

Polyurethanes are also used in protective coatings to which they impart solvent and chemical resistance, hardness, and weather resistance. One type of coating resembles an alkyd (Section 11.1.2) and is formulated in the same way except that the di- or triisocyanate replaces the alkyd's phthalic anhydride. Toluene diisocyanate or 4,4'-diphenyldimethylmethane diisocyanate may be used, depending on the application. Hexamethylenediisocyanate (HMDI) has good weathering properties and color retention, and is used where appearance is important. Thus a critical application is for airplane coatings. The isocyanate is used as a so-called biuret trimer (see above). The biuret trimer is reacted with a hydroxyl-containing coreactant to provide the coating for most of the commercial and military airplanes in the world. It replaced an earlier coating based on epoxy resins.

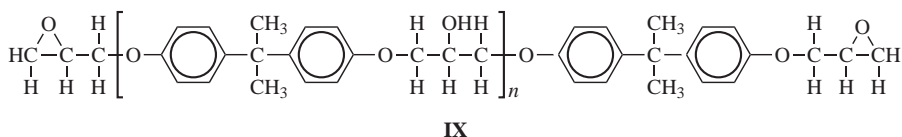
17.4.3 Epoxy Resins

The curing of epoxy resins is interesting because functionality is generated in the course of the reaction.

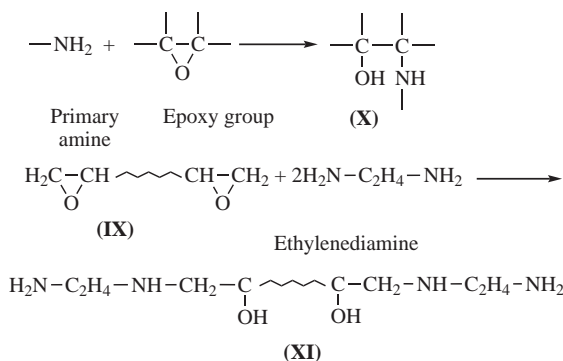
Epoxy resins are typically condensates of bisphenol A with epichlorohydrin. If a large excess of epichlorohydrin is used a simple molecule results from the condensation of 2 moles of epichlorohydrin with 1 mole of bisphenol A.



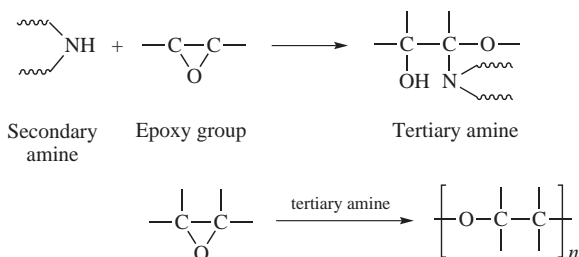
If the reactants are close to equimolar, on the other hand, an oligomer (**IX**) is formed where n is between 1 and 4. In either case the terminal groups are epoxy groups.



The epoxy groups will react with di- or multifunctional amines such as ethylenediamine or diethylenetriamine to give a crosslinked resin. When one of the primary amine groups reacts with an epoxy group, a hydroxyl group and a secondary amine group are generated (**X**). Both of these groups can react further with epoxy groups in principle, although the hydroxyl group will react only at high temperatures. The aliphatic amine groups react at room temperature, and if two molecules of ethylene diamine react with one polymer molecule of epoxy resin a molecule (**XI**) is generated with four amine groups – two primary and two secondary. The new polymer has four amine groups with six active hydrogens, each of which can react with more epoxy resin, and thus the conditions for crosslinking have been established.



The interaction of the secondary amine group with an epoxy group generates a tertiary amine. Tertiary amines are catalysts for the self-polymerization of epoxy groups to polyethers, so yet another polymerization mechanism comes into play and is shown in the following equation. This polymerization is chain growth, whereas the polymer formation resulting from the condensation of amine and epoxy groups is step growth.



17.4.4 Dendritic and Hyperbranched Polymers

Dendritic polymers are a special class of macromolecules and their production represents the ultimate in step growth polymerization, in that each step is carried out separately. A linear polymer consists of long chains of monomer, sometimes coiled and tangled, sometimes ordered laterally in a crystalline domain. A dendrimer, on the other hand, consists of molecular chains branching out from a common center, and there is no entanglement between them. The first dendrimer was synthesized by Vögtle in 1978 and is typical. It involves a Michael condensation of acrylonitrile to primary amine groups, for example, aniline (**XII**). The initial reaction (Fig. 17.11)

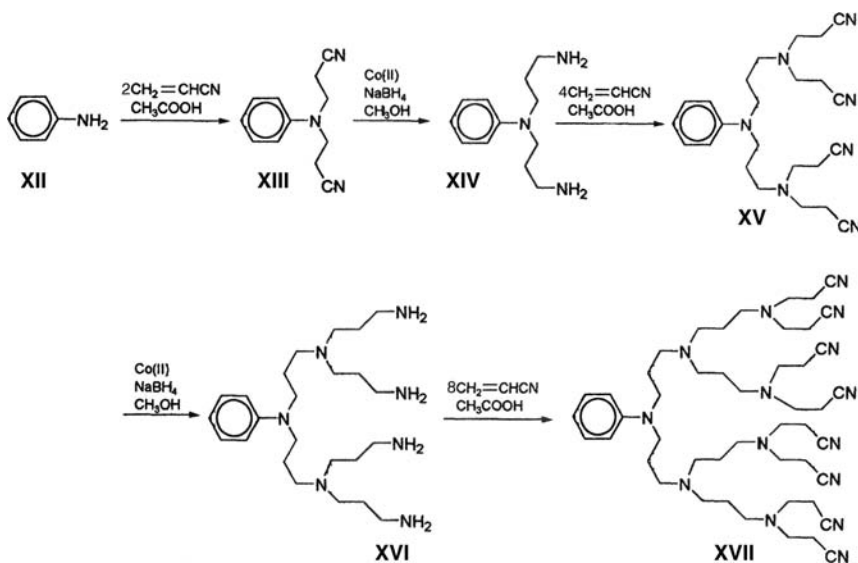


FIGURE 17.11 Vögtle's synthesis of poly(propyleneimine).

gives a dicyano compound (**XIII**), and these groups are reduced to amine groups (**XIV**). The Michael condensation is repeated to give four cyano groups; reduction gives four amino groups and so on, until a spherical polymer molecule is obtained with amine groups at its surface. The starting molecule is said to be the zero generation dendrimer. Structure **XII** is said to be first generation, **XIII** is second generation, **XIV** is third generation, and so on until the terminating generation. The molecular weights of dendrimers increase exponentially with the number of generations. The molecular weights of the zeroth, first, second, third, and fourth generation poly(propyleneimine)s are, respectively, 93, 209, 437, 893, and 1805. The molecular weight of dendrimers is limited by steric factors, that is, overcrowding at the molecule surface. This is called the starburst effect. Molecular weight can also be limited by the use of terminating reagents that have no further functional groups to react. They may have other properties instead. Figure 17.12 shows a fifth generation poly(propyleneimine) with

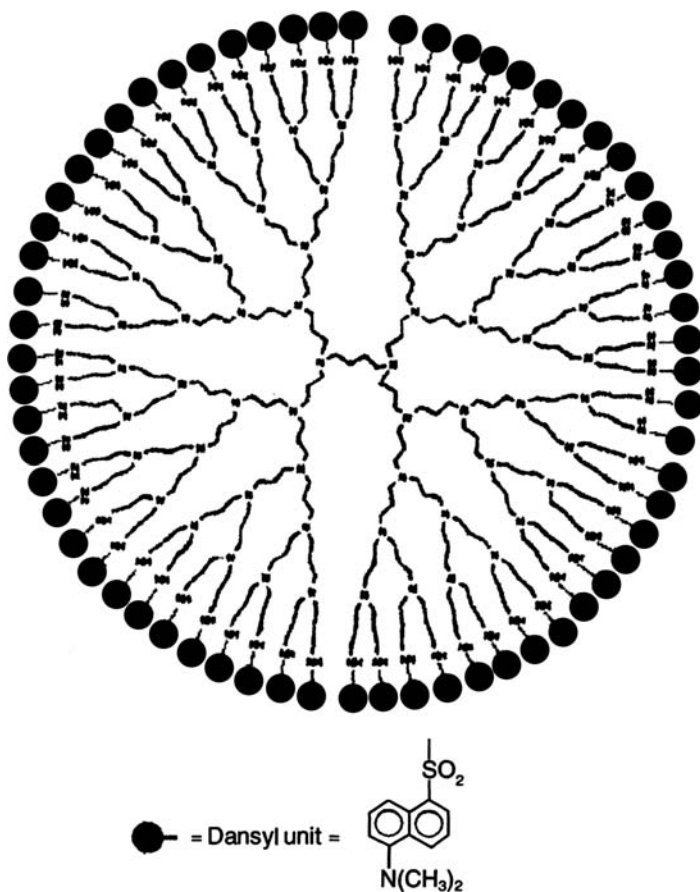


FIGURE 17.12 A fifth generation poly(propyleneimine) dendrimer with 64 strongly fluorescent units at its periphery. [Source: V. Balzani in M. Freemantle, *Chem. Eng. News*, **77**(44), 27, 1999.]

butylenediamine at its core and with 64 strongly fluorescent dansyl units at its periphery. This method of making dendrimers is called divergent. Convergent polymerization is also possible, where one starts with the groups that are to appear at the surface and links them backwards to the inner unit and finally to a central core molecule. Either method requires polymerization to be brought about step by step as each successive generation is added. Monomers are prevented from undergoing more than a single step in the polymerization process by requiring a change in functional groups, as occurs with the conversion of nitrile to amine groups in Figure 17.11. A consequence is that dendrimers are inevitably expensive to make, although the automatic synthetic methods devised for protein synthesis and combinatorial chemistry can be invoked. If functional groups were not changed, then unbridled polymerization would take place to give less regular but still highly branched polymers known simply as hyperbranched polymers.⁸ These share some of the characteristics of dendrimers and are much easier to make. Their closeness to dendrimers is measured by their molecular weight distribution (Section 17.3.4). Dendrimers have a distribution of unity. The second generation hyperbranched polymer shown in Figure 17.13 is made from 1,3,5-benzenetricarboxylic acid (**XVIII**) at its core, an aminodicarboxylic acid as monomer (dendrone) (**XIX**) and diethylamine as capping agent. A molecular weight distribution of 1.2 is claimed.

Dendrimers and hyperbranched polymers differ from linear polymers in their properties. Some of these are shown in Table 17.5. As with radial block polymers (Section 17.3.6) viscosities are lower because there is no tangling of chains and solubilities higher because of the number of sites for solvation. Crystallinity is low because there is no scope for alignment of polymer chains or interaction between them, and reactivity is high unless terminating agents have blocked the surface of the dendrimer. The spherical structure combined with the lack of polarity means that dielectric constants are often lower than 2 compared with 4–6 for most linear polymers.

The synthesis of dendrimers and hyperbranched molecules is a fascinating extension of polymer technology. Dendrimers are at present in the situation that lasers were about 1960; that is, they are answers in search of a problem. There are potential medicinal applications in drug delivery systems, in which the drug is loosely bonded to the dendrimer so that it can be released by heating, enzyme action, or photochemically. The dendrimer itself can be made water soluble, for example, by surface carboxyl groups, while still retaining a water-insoluble drug. Additional functional groups can be attached that will bond to the target organ. Poly(amidoamine) dendrimers (PAMAM) are transfection agents that are effective in transferring genetic materials into the cell. They also have application as immunodiagnostic agents. They are available commercially under the trade name “Starburst.”

Pharmaceutically active compounds can easily be encapsulated into the interior of dendrimers or chemically attached or physically adsorbed onto its surface. At present the main application is attachment of anticancer drugs. For example, toxicity to healthy cells of doxorubicin attached to “Starburst” was reduced by 80–98% compared with the free drug, yet it was successfully taken up by several cancer cell lines.⁹

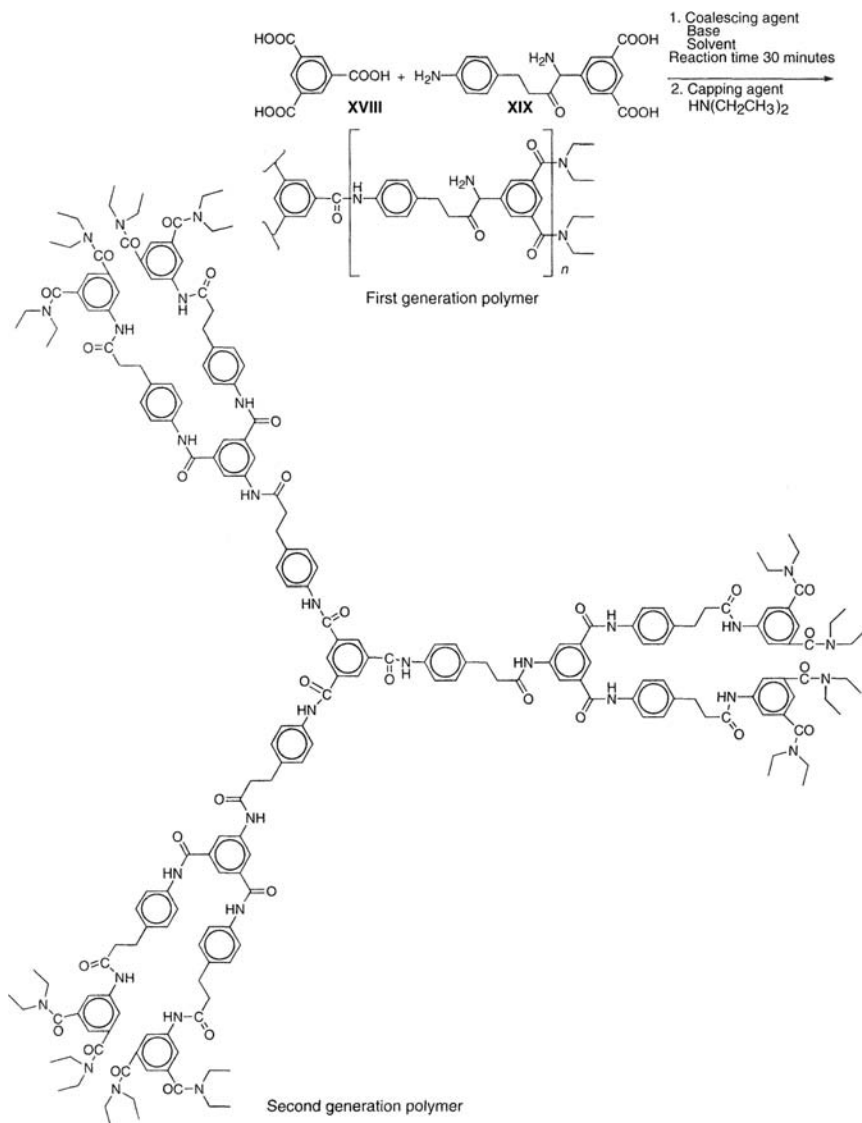


FIGURE 17.13 Second generation hyperbranched polymer from 1,3,5-benzenetricarboxylic acid and an aminodicarboxylic acid dendrone.

Polyether dendrimer films can occlude metal ions, and functional groups on the surface of dendrimers can be arranged to detect organic compounds selectively. Dendrimers made by the convergent method can be made unsymmetrical with hydrophilic groups at one side and hydrophobic groups at the other, and these will form monolayers at interfaces. Large dendrimers can behave as single molecule micelles.

TABLE 17.5 Properties of Linear Polymers and Dendrimers

Property	Linear Polymers	Dendrimers
Shape	Random coil	Spherical
Viscosity	High	Low
Solubility	Low	High
Crystallinity	Depends on polymer	Low
Reactivity	Low	High
Compatibility	Low	High
Compressibility	High	Low
Structural control	Low	Very high
Dielectric constant	Ultralow, <2	Typically 4–6; polyethylene = 2.26

Dendrimers can be made with light-absorbing groups at their peripheries and can therefore harvest successive quanta of light, as occurs in photosynthesis. This energy can transform into chemical energy for reactions or electric current, or it can be converted to monochromatic light. A laser dye has been placed in the dendritic core and the system acts like an optical amplifier. Another potential application is the use of the dendrimer as a host for polymerization, which can occur in the cavities of the dendrimer, thereby avoiding termination with other polymerization chains. Finally, dendrimers have ultralow dielectric constants, which could lead to breakthroughs in semiconductor performance.

There is empty space within dendrimers in the forms of voids and channels, and these offer the possibility of catalytic reactions similar to those brought about within zeolites. Dendrimers provide unique catalytic environments both at their surface and in the cavities. They can provide a microenvironment for molecular reactions and nanoscale reactor sites for catalysis. This is discussed further in Section 18.9.

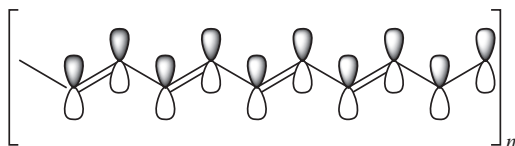
Janus dendrimers are a highly branched bifunctional class of dendrimers. They are two-faced (hence the name from the two-faced Roman God) with polar groups on one side and nonpolar groups on the other. It was found recently that when they are added to water they unexpectedly self-assemble into tiny bubbles and structures called dendrimersomes. These, because of their structure, might be more suitable for medical applications than dendrimers made from phospholipids and polymers. The dendrimersomes that form from the Janus dendrimers assume vesicle, tube, and disk shapes. These shapes can conceivably accommodate guest molecules and thus would be capable of participating in drug delivery. It will be interesting to observe the development of the dendrimersomes.¹⁰

17.4.5 Conducting Polymers

The polymers so far discussed in this book have been insulators; indeed, many of their applications depend on low electrical conductivity. This can also create problems, for example, in hospital operating rooms, where it is essential that static charges do not build up and lead to sparking and explosions involving anesthetics. This can be

inhibited by addition of graphite or a similar conducting material to the polymer mix, but there has been growing interest in inherently conducting polymers.^{11–13} These may be ionically conductive, for example, poly(ethylene oxide) containing lithium perchlorate (LiClO_4), which is used as a solid phase electrolyte in batteries. Of greater interest, however, are intrinsically conductive polymers.

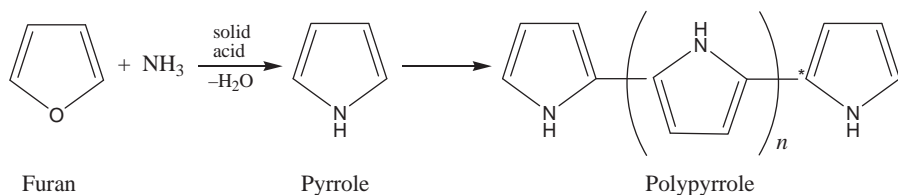
Typically, chain growth polymers are bound by sp^3 covalent bonds. In this form of hybridization, the electrons have low mobility and are insulating. The valence bands and conduction bands are widely separated. Conducting polymers, in contrast, contain conjugated double bond systems. The carbon backbone is linked by sp^2 hybrid bonds and each carbon atom carries an electron in a p_z orbital. Thus polyacetylene would have the structure



As such, it is a silver nonconducting film, with a filled valence band and no accessible conduction bands. Oxidation with iodine, however, withdraws electrons from the π electron clouds and the remaining electrons form a one-dimensional electronic band, to give a so-called p -type semiconductor. The electrons within this band become mobile when it is partially emptied, and the material approaches the conductivity of silver, the best metallic conductor. In principle, a reducing agent could add electrons to an otherwise unfilled band to give an n -type semiconductor, but in practice this is rarely done. Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid were awarded the Nobel Prize in 2000 for work on conducting polymers begun in 1976.

Conjugated polymers can be made with anionic, cationic, free radical, and Ziegler–Natta initiators. The last are especially valuable for designating particular stereochemistry for the polymers. Polyacetylene is generally not prepared from acetylene but from cyclooctatetraene or related compounds by a ring-opening metathesis polymerization (Section 4.14) with a range of catalysts such as ruthenium chloride in alcohol or of the type $\text{Mo}(=\text{CHBut})(\text{NAr})(\text{OR})_2$. Doping can be carried out subsequent to the polymerization with reagents such as AsF_5 , SbF_5 , NOPF_6 , and FeCl_3 .

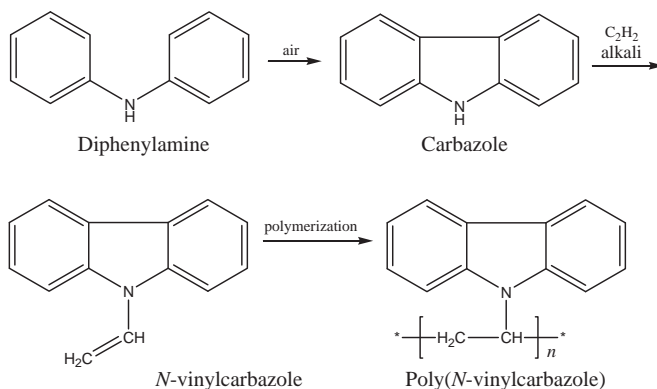
Polypyrrole and polyalkylthiophenes are significant conducting polymers. They are polymerized by oxidation, and excess charge is formed in the reaction. Water is eliminated. Pyrrole is prepared from furan (Section 16.2) by treatment with ammonia over a solid acid catalyst. It is polymerized in aqueous solution with ammonium persulfate. Dodecylbenzenesulfonic acid is used as a dopant and the polymer is precipitated by addition of methanol.



Polyalkylthiophenes are similarly prepared by oxidative polymerization of alkylthiophenes with ferric chloride, unless a regioregular compound is required, in which case more complicated methods must be used.¹⁴

Aniline has been oxidized for over a century to a black pigment, aniline black, and used in printing inks and black shoe polish. Chlorates and hypochlorites bring about the change. Modification of this process gives a conducting polymer.

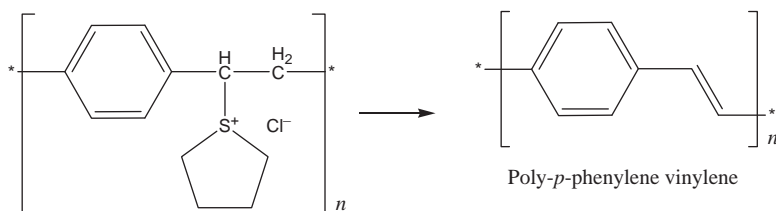
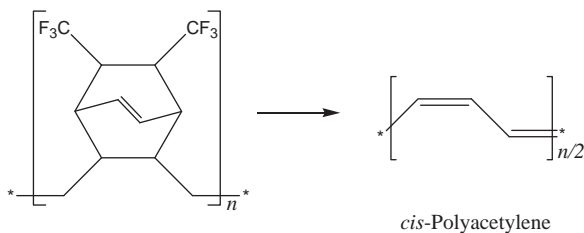
A photoconducting organic polymer of commercial significance is poly(*N*-vinylcarbazole). It is prepared by polymerization of *N*-vinylcarbazole, which in turn is formed from carbazole and acetylene under alkaline conditions. Carbazole comes from air-oxidation of diphenylamine:



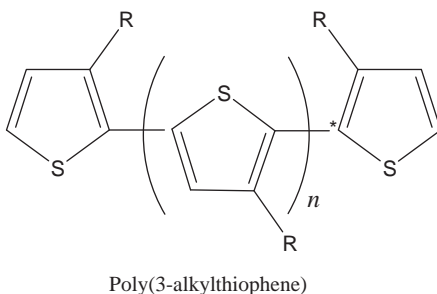
It becomes conducting when illuminated with visible light and is used in photocopiers. The earliest photocopiers depended on drums or moving belts of silicon or selenium, which are both semiconductors. In the modern version, a drum or belt coated with poly(*N*-vinylcarbazole) is given a surface electric charge. The image to be copied is projected onto the drum. The areas exposed to light become conducting, and their charge drains away. The dark areas retain their charge. The drum is then brought into contact with toner, which adheres to the charged areas. This image is transferred to paper and the toner baked on.

Poly(*N*-vinylcarbazole) has the advantage that it is truly thermoplastic; that is, it softens at the moderate temperature of 150°C. This is not true of many conducting polymers, and in general they have poor processability, low solubility in organic solvents, and instability to moisture. They are also expensive. For these reasons, although they have been on the brink of achieving commercial importance for thirty years, progress has been slow.

One way to avoid the processability problem is to polymerize a nonconjugated monomer to give a polymer, which is then fabricated and converted to the conjugated polymer. Such materials are called precursors. The precursor for acetylene is a di(trifluoromethyl) derivative of bicyclo[2.2.2]oct-2-ene, which is deposited, for example, on an electrode. On heating to 60°C, it gives regioregular *cis*-polyacetylene. The precursor for poly-*p*-phenylene vinylene has tetrahydrothiophene as the group displaced on heating. It can be processed because its side groups make it soluble.



Poly(*p*-phenylene vinylene) and its soluble derivatives are seen as prototypical electroluminescent semiconducting polymers; poly(3-alkylthiophenes) are the archetypical materials for solar cells (Sections 20.3.3.2 and 20.3.3.3) and transistors. Polyaniline has served as anode and with a lithium–aluminum alloy as cathode in a 1.6 mm thick battery weighing 1.7 g. Organic light emitting diodes (OLEDs) based on conducting polymers offer hope of television, phone, and computer screens that are thinner and have better picture quality and greater energy efficiency than present screens. The drawback is that present designs are expensive to make and recycle because they require an indium tin oxide electrode.



Such electrodes can sometimes be replaced by the conducting polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS). This is a macromolecular salt made up of sodium polystyrene sulfonate with poly(3,4-ethylenedioxythiophene) (Fig. 17.14). It is transparent, conducting and ductile and is used, among other things, for coating photographic films to reduce static.

Graphene, which won the 2010 Nobel Prize for physics for Andre Geim and Kostya Novoselov, is a single-atom-thick sheet of carbon atoms linked by sp_2 bond. It is the ultimate in aromatic chemistry and in conducting polymers. It is transparent and may

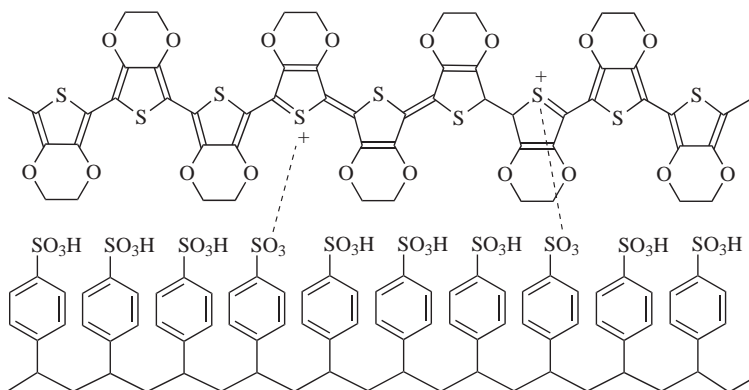


FIGURE 17.14 Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS).

(or may not) achieve significant industrial applications. In 2007, engineers at the University of Southern California reported the large scale production of highly transparent graphene films by chemical vapor deposition. Carbon atoms were first deposited on a nickel plate from methane gas. A protective layer of thermoplastic was then placed on top of the film and the nickel underneath dissolved in an acid bath. The plastic-protected layer was then attached to another polymer sheet, which could be incorporated into an organophotovoltaic cell. These graphene sheets can already be created in sizes of over 100 cm², and this might be a route to printable arrays of solar cells for such applications as touchscreens, liquid crystal displays, and organic light-emitting diodes (Section 20.3.3.3).^{15,16}

A light-emitting electrochemical cell has been demonstrated with a graphene cathode and a PEDOT anode, and in another assembly with a graphene anode.¹⁷ These novel light-emitting devices did not involve metals.

Methods of production of graphene and related all-carbon structures such as nanotubes are not polymerization procedures, and the multitudinous possible uses of graphene are both some distance in the future and beyond the scope of this book.

17.4.6 Conducting and Semiconducting Inks

Conducting inks can be made like conducting polymers by inclusion of conducting materials into a nonconducting polymer formulation.¹⁸ With inks, the conducting medium is often silver, silver oxide, or copper. Carbon, graphite, platinum, gold, copper, cobalt, and palladium may also be dispersed as nanoparticles in polymer media.

The polymer matrix is frequently an epoxy resin, which requires curing by heating, ultraviolet light, or other standard methods. The inks are solvent-based. However, water-based formulations are available as are hot melt formulations. Conductive inks may be used for various types of printing including flexographic and gravure for flexible films, screen, offset, and inkjet. Thus they may be used on both rigid and flexible substrates. This means that the comparatively cumbersome printed circuit can

be replaced by a flexible, printed film. Accordingly, printed electronics are experiencing considerable growth in the 2000s. This is at the expense of the traditional printing industry that is nonetheless recouping its losses by way of the newfound flexible, printed films.

One exemplary use of silver-based conductive inks is for radiofrequency identification (RFID) tags. These tags contain antennae that allow them to receive and respond to radiofrequency signals from an RFID transceiver. The tag may be inserted below the skin of a pet whose location is then readily identified. The tags are useful for tracking books from libraries and stores, airline baggage, identification badges, trucks and trailers, and containers and pallets. Cards in which are embedded RFIDs can be used to pay transportation fees such as for toll plaza passage. Computer keyboards contain membranes with printed circuits that sense when a key is pressed.

The electronic components that offer a home to conductive printing inks include capacitors, diodes, resistors, and transistors as well as complete circuits such as sensors, keypads, electrodes, and a variety of electroluminescent displays. End-use applications include photovoltaics, medical devices, flexible displays, energy storage, and advanced types of packaging.

The complementary metal oxide semiconductor (CMOS) technology conventionally used to make chips is expensive and requires a solid base such as silicon to manufacture circuits. Current interest is in the use of printing inks based on polythiophene nanoparticles that would permit displays to be rolled up or bent round corners.

17.5 POLYMER PROPERTIES

In the previous section we described how monomers were converted to polymers, bifunctional monomers leading to linear thermoplastic resins and polyfunctional monomers providing crosslinked thermosetting resins. Only one property, average molecular weight, has been mentioned. Molecular weight and mechanical strength are related since strength increases rapidly between 50 and 500 monomer units. Further increases in molecular weight have little effect. In this section we describe additional properties of polymers and discuss the factors that give them the properties that make them useful – high viscosity, tensile strength, and toughness.

17.5.1 Crystallinity

Crystallinity is the key factor governing polymer properties. An easy way to visualize it is to regard crystallinity as a situation in which the polymer chains fit into an imaginary pipe. That is, they align themselves in bundles with a high lateral order, and the chains lie side by side. To do this they must be linear, not coiled, and there must not be bulky groups or branching to prevent the polymer chains from achieving molecular nearness.

There is an analogy, although not an exact one, with the crystallization of nonpolymeric materials like sodium chloride or *n*-hexane where the ions or

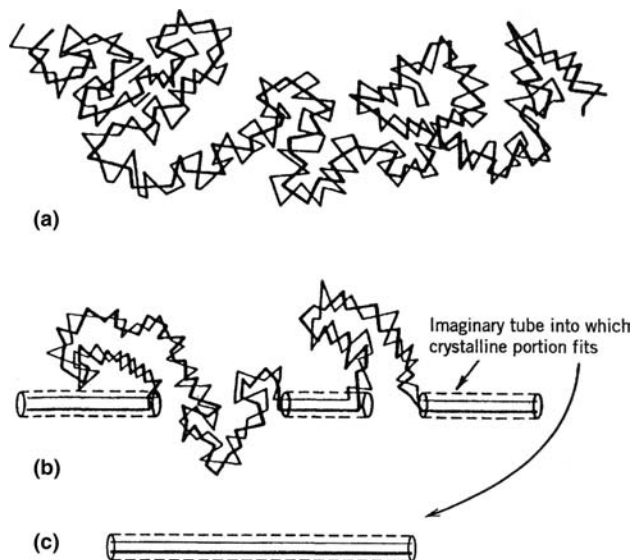


FIGURE 17.15 Polymer crystallization: (a) noncrystalline, (b) partially crystalline, and (c) completely crystalline.

molecules must fit into a crystal lattice. With polymers, however, it is long chain molecules, not ions or small molecules, that must fit, and the structure into which they fit is not a lattice but an imaginary cylindrical tube. Figure 17.15 attempts to illustrate this concept and shows how the chains may line up in an ordered fashion. It is, however, unlikely that all the chains in a polymer or even all of a single chain will be able to enter into the ordered structure of complete crystallinity, although nylon and high density polyethylene come close. Usually the ordered regions are small – microcrystalline – and are scattered through the polymer which is otherwise amorphous. Where the polymer is crystalline, it is plate-like and of uniform thickness. Emanating from these crystalline regions are the sections of the chains that are not incorporated into the crystal lattice. They form the amorphous part of the polymer and may actually coil back over the crystalline platelets. Thus one can legitimately talk of the degree of crystallinity of a polymer. Some polymers are almost totally crystalline, others almost totally amorphous. Even a single polymeric substance can exist with a range of crystallinities depending on how it was made and processed.

Two factors govern the tendency of a polymer to crystallize. One is the ease with which the polymer chains will pack into a “crystal,” and the other is the magnitude of the attractive forces between neighboring molecules of the polymer. The first of these means that crystalline polymers are more likely to form from chains that do not have bulky substituents, and where there is not a great deal of branching. Poly(ethylene terephthalate) is without bulky side chains and is crystalline after orientation, that is, after the fibers are drawn. The rigid benzene ring makes the polymer chains stiff and unwilling to coil.

Isotactic polymers made by Ziegler–Natta polymerization are also highly crystalline unless, as in *p*-substituted polystyrenes, a bulky group keeps the polymer chains apart. Polystyrene, polymerized as it normally is by peroxide catalysis, is an example of an amorphous polymer. Isotactic polystyrene made by Ziegler–Natta catalysis, however, is highly crystalline with better properties between its glass transition temperature (about 80°C) and its crystalline melting point (about 240°C). Its commercialization was inhibited because it crystallizes very slowly and therefore changes its properties after processing. However, metallocene catalysts (Section 17.3.12) were thought to have made possible a syndiotactic form with a high melting point that would function as an engineering polymer, that is, one that would replace metals. Dow discovered various difficulties and aborted their development effort.

Other amorphous polymers are exemplified by poly(methyl methacrylate) and polycarbonates. The latter are condensates of bisphenol A and phosgene (Section 9.1.2.2). The pendant groups on the methacrylate polymer are bulky, and the two phenyl groups in the polycarbonate are not coplanar. Thus crystal formation is obstructed. Most copolymers have little crystallinity because their structures are nonlinear.

In general, crystalline polymers are opaque because light is reflected or scattered at the boundaries between the microcrystalline and amorphous regions. Amorphous polymers are transparent and glass-like. Two exceptions should be noted. If a crystalline polymer is biaxially oriented, that is, stretched simultaneously in two directions, as in drawn poly(ethylene terephthalate) (Mylar) sheet, then the whole sheet is in effect a single crystal and is transparent. Furthermore, in a few polymers, the most important of which is the polymer from 4-methyl-1-pentene, the refractive index of the crystal is identical with that of the amorphous region. No light scattering occurs at boundaries, and the crystalline polymer is clear.

The second factor leading to crystallization is the forces of attraction between neighboring molecules. These comprise hydrogen bonding, which is the strongest, and the various kinds of Van der Waals forces, dipole–dipole forces, dipole-induced dipole forces, and London dispersion forces. They vary in strength from about 1–2 kcal/mol (5–10 kJ/mol) per unit of polymer chain in elastomers to 5–10 kcal/mol (20–40 kJ/mol) in fibers. London forces are weak, whereas the others can be quite high. Cellulose and nylon provide examples of hydrogen bonding, PVC, and polyacrylonitrile of dipole–dipole interaction, and polyethylene of London forces.

We can extend the analogy between crystallization of *n*-hexane and polyethylene. As *n*-hexane is cooled, the thermal motion of the molecules decreases until it can no longer overcome the forces of attraction between them. Accordingly, the molecules pack into the orientation of lowest energy, that is, the crystal lattice, and the sample solidifies or crystallizes.

The molecules of polyethylene are hundreds of times larger than those of hexane. Although the intermolecular forces between the $-\text{CH}_2-$ units are about the same in the two molecules, the total force per molecule in the polymer will be much higher. Furthermore, the polyethylene chains will not have the freedom of movement of hexane molecules. Instead, they will be wriggling and coiling. There is little chance

that one of them will ever be fully extended. The chains will also become entangled with one another, which will hinder molecular motion. Molten polymers are viscous both because of chain entanglement and intermolecular forces. The latter factor is negligible at high temperatures, and viscosity under these conditions is due largely to chain entanglement.

When the temperature of molten polyethylene is reduced, molecular motion diminishes as it does in hexane. Eventually there will be a tendency for the chains to pack into a crystal lattice. In order to do this they will need to be extended and not coiled, but the chance of a chain being fully extended is small. There will, however, be large portions of polymer chains that are extended. These will pack into an ordered crystal lattice and provide the microcrystalline regions, while the tangled, coiled portions will form the disordered amorphous regions seen in Figure 17.15.

In block copolymers (Section 17.3.8) it is possible to create a block that is highly crystalline together with one that is amorphous to obtain a final copolymer with special properties.

Crystalline polymers usually have greater mechanical strength and higher melting point than amorphous polymers. Because the chains in the crystalline regions are closely packed, they would also be expected to have higher densities, and this too is observed. For example, low density polyethylene has a tensile strength (Section 17.5.4) of 2000–2500 psi (140–175 kg/cm²), a softening point of 85–87°C, and a specific gravity of 0.91–0.93. High density polyethylene, on the other hand, has a tensile strength of 3500–5500 psi (245–385 kg/cm²), a softening point of 127°C, and a specific gravity of 0.94–0.97.

The degree of crystallinity of a polymer is measured by X-ray diffraction by the same technique used for single crystals. High density polyethylene may have as much as 90% crystallinity; the low density material has only about 55%, which is still high considering the extent of chain branching in the polymer. It occurs because the lengths of polymer chain between the branches are capable of getting close enough to other chains for crystallization to take place.

Crystallinity is also related to orientation. If one slowly flexes a wide rubber band, an appreciable amount of heat is generated, which can be felt if the band is touched to the lips. This results from the friction of one polymer molecule rubbing against another as the stretching action causes them to align. Before it is stretched, the rubber band is largely amorphous. The alignment on stretching is tantamount to crystallization, which also causes the translucent rubber band to become opaque. Orientation of the polymer has caused it to crystallize. The heat generated can therefore also be thought of as heat of crystallization. The degree of crystallinity that can be induced in an elastomer by stretching can reach 30% (Fig. 17.16).

The orientation or crystallization of polymer molecules by stretching or drawing is an important step in the processing of polymers for use as textile fibers. When nylon and polyesters are manufactured they have low crystallinity. The stretching or drawing of the fibers causes the polymer molecules to line up or crystallize to give the longitudinal strength required in fibers.

A difference between fibers and rubbers is that the latter have much greater “elastic memory” and do not remain stretched and crystalline. In other words, it is

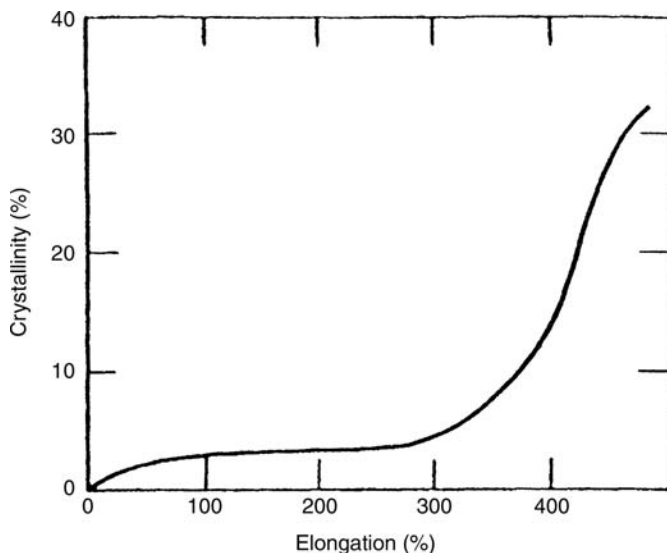


FIGURE 17.16 Crystallization of cured rubber by stretching.

hard to stretch them beyond their limit of crystallinity. The reason is that rubber is lightly crosslinked, and these crosslinks tend to pull the rubber molecules back to their original configuration. In addition, stretching is a disorder–order transition, and the entropy decreases. The return to the unstretched state is favored by the corresponding entropy increase. In nylon the “crosslinking” takes the form of hydrogen bonds that break and reform as the fiber is stretched. Indeed, stretching orients the molecule so that more hydrogen bonds are formed than are broken. Consequently, the elastic memory is quickly exceeded on stretching.

17.5.2 Glass Transition Temperature, Crystalline Melting Point, and Softening Temperature

If an amorphous material such as polystyrene is melted and then allowed to cool, it does not solidify sharply. First it goes from a viscous liquid to a rubbery solid, then to a leathery solid. Finally, when all of the molecules have lost their thermal “wriggling” motions, it becomes a glassy solid, recognizably polystyrene. The last change is a sharp one, and the temperature at which it occurs is called the glass transition temperature of the polymer, T_g . Obviously it has a bearing on the properties of the polymer at the service temperature at which it is to be used. A polymer that is a soft, leathery material above its T_g may be hard, brittle, and amorphous below the T_g .

The glass transition temperature is associated primarily with amorphous polymers, although crystalline polymers also have a glass transition temperature, because all polymers have amorphous regions between the microcrystalline regions.

TABLE 17.6 Typical T_g and T_m Values for Polymers

Polymer	Temperature ($^{\circ}\text{C}$)	
	T_g	T_m
<i>cis</i> -Polybutadiene	-101	4
<i>cis</i> -Polyisoprene	-73	29
<i>trans</i> -Polyisoprene	-58	70
Linear polyethylene	-70 to -20	132
Polypropylene	-16	170
<i>trans</i> -1,4-Polybutadiene	-9	139
Nylon 66	47	235
Poly(methyl methacrylate)	49	155
Poly(vinyl chloride)	70	140
Polystyrene	94	227
Polycarbonate	152	267
Cellulose triacetate	111	300
Poly(tetrafluoroethylene)	135	327

If a crystalline polymer is used above the T_g of the amorphous regions, the latter will be flexible, and the polymer will be tough. If the temperature is below the T_g , however, the amorphous regions will be glassy and the polymer brittle. A similar situation for block copolymers is described in Section 17.3.8.

The temperature at which a molten polymer changes from a viscous liquid to a microcrystalline solid is called the crystalline melting point, T_m , of the polymer. If the solid polymer is partly crystalline, the change is accompanied by sudden changes in density, refractive index, heat capacity, transparency, and similar properties. It is analogous to the melting point of a nonpolymeric chemical compound but is not as sharp, and melting and freezing take place over a small range. The value of T_m depends on chain structure, intermolecular forces, and chain entanglement.

The softening point is an arbitrary measure of the temperature at which a polymer reaches a certain specified softness. It is of great importance as the upper service temperature of a polymer but has little significance on the molecular level.

Table 17.6 indicates typical values for the glass transition temperature and crystalline melting point for various polymers. T_g is about one-half to two-thirds of T_m for most polymers if the temperatures are in degrees absolute. Deviations from this may be due to unusual molecular weight distributions, chain stiffness, and symmetry. These values, unlike the melting points of pure organic compounds, can be considered only "typical." The glass transition temperature may vary with the molecular weight of the polymer, its method of preparation, its end group distribution, and the degree of crystallinity in a given polymer sample. For a completely unoriented material the glass transition temperature will be very low. When the material is oriented or converted to a crystalline state, the glass transition temperature increases. The glass transition temperature for poly(ethylene terephthalate) may vary from -80°C to 180°C .

17.5.3 Molecular Cohesion

Molecular cohesion is the average force between the repeating units of a polymer chain and its neighbors. The forces are Van der Waals forces or hydrogen bonds. Their magnitude can be calculated from a parameter called the cohesive energy density δ^2 . It can be calculated from the latent heat of vaporization, δH_v (cal/mol), or the surface tension, ρ (dynes/cm), by the relationships

$$\delta^2 = \frac{\Delta H_v - RT}{M/D} = \frac{14\rho}{(M/D)^{1/3}}$$

where R is the gas constant (1.987 cal/mol·K; 8.314 J/mol·K), T is the absolute temperature, M is the molecular weight, and D is the density (g/cm³). The units of δ^2 are cal/cm³ and those of δ are cal^{1/2}/cm^{3/2}. The latter unit is called the hildebrand.

Hydrogen bonds contribute most to molecular cohesion. Dipole–dipole forces contribute less, and London dispersion forces the least. The strength of the molecular interactions diminishes rapidly, actually with the sixth power of the distance between the molecules. Thus bulky amorphous polymers have relatively low intermolecular forces whereas those in crystalline polymers are much higher because the molecules are much closer together.

17.5.4 Stress–Strain Diagrams

Many of the quoted properties of polymers are derived from stress–strain diagrams. These are graphs of the deformation in a polymer sample (expressed as percent of elongation) produced by a particular applied stress (a tension expressed as pounds per square inch, grams per square centimeter, or meganewtons per square meter). Such diagrams can be generated quickly from a given polymer sample of controlled size in a testing laboratory. For reproducibility, a standard sample and rate of extension must be used. An example (for a hard, tough plastic) is shown in Figure 17.17.

In the initial stages of the extension, the stress–strain diagram is linear. That is, the material obeys Hooke's law, and stress is proportional to strain. The gradient or slope of this straight section is called the initial modulus of elasticity and is a measure of the stiffness of the material (Young's modulus). If the applied stress is removed at this stage, the polymer will return to its initial length. After a certain stress, the graph ceases to be linear, and the extension is nonreversible; that is, a permanent deformation is produced. The yield point is defined as the maximum in the stress–strain curve, as shown in the diagram, and has an elongation at yield and a yield stress associated with it. Some authorities define the yield point as the point at which deformation becomes irreversible, that is, at which Hooke's law ceases to be obeyed. Because many polymers do not obey Hooke's law, the modulus is frequently expressed as pounds per square inch or meganewtons per square meter of tensile strength at a given degree of elongation such as 2%. This is called the 2% modulus. Some elastomers are better described by a 100% or 300% modulus.

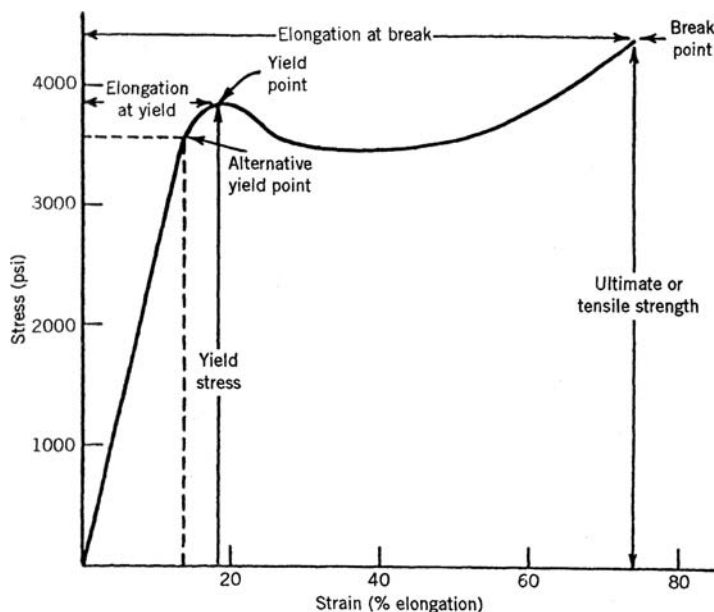


FIGURE 17.17 Stress-strain diagram.

After the yield point, the plastic stretches relatively easily and, after stiffening a little toward the end, it breaks, and the curve comes to an abrupt end. The break point has associated with it an elongation at break or upper limit of extensibility and an ultimate tensile strength. The area under the curve up to the break point may be measured and is called the work-to-break. The tensile strength is the strength required to pull the polymer apart, and the work-to-break is a measure of the ability of the polymer to resist not only tension or “pulling apart” but also other stresses such as bending, compression, impact, and twisting.

Figure 17.18 shows the type of stress-strain diagrams obtained for fibers, thermoplastics, and elastomers. Fibers, because they have been oriented, have high tensile strength and modulus and resist elongation. The work-to-break is small, although the polymer is strong and resists “pulling apart.” The elastomer, on the other hand, has high elongation but low tensile strength and modulus. Thus it has little resistance to deforming forces other than elongation. As its extension is reversible, a return stress-strain curve can be obtained if the stress is reduced before the sample breaks. This is indicated by the dotted line. The area within this hysteresis loop is the work dissipated as heat during the cycle.

The thermoplastic shown has quite a high modulus and tensile strength and a fairly high elongation. The area under the curve is large; hence this type of thermoplastic would be used if a wide variety of deforming forces were expected, whereas a fiber would have best resistance to simple tension. Elastomers are useful because they “bounce back” and can absorb energy by hysteresis.

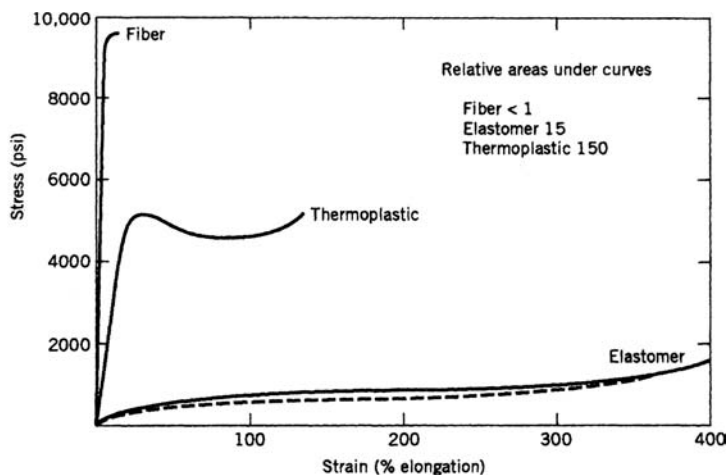


FIGURE 17.18 Stress-strain curves.

17.6 CLASSES OF POLYMERS

Polymers are used in five main ways: as elastomers, plastics, fibers, surface coatings, and adhesives. Table 17.7 shows the combination of polymer properties required for the first three applications in terms of the four major properties.

Elastomers have a low modulus. Modulus is a measure of stiffness, and rubbers are not stiff. On the other hand, they need to be highly extensible, and elongations of 1000% are common. The crystallinity of an elastomer is low when the material is unstressed, but stretching leads to a higher degree of crystallization (Section 17.5.1).

TABLE 17.7 Polymer Properties

Property	Elastomers	Plastics	Fibers
Modulus (psi)	15–150	1500–200,000	150,000–1,500,000
Modulus (kg/cm ²)	1–10	100–14,000	10,000–100,000
Extensibility, upper limit (%)	100–1000	20–100	<10
Crystallization tendency	Low when unstressed	Moderate to high	Very high
Molecular cohesion (cal/monomer unit)	1000–2000	2000–5000	5000–10,000
Examples	Natural rubber, polychloroprene, polybutadiene	Polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(vinyl acetate)	Silk, cellulose, nylon, polyester, acrylics, polypropylene

Molecular cohesion in elastomers must be low because otherwise the polymer chains will not easily slip over one another when the elastomer is stretched or slide back reversibly when the tension is released.

The second class of polymers is plastics. These are defined as polymers or resins that have been made into shapes, usually under pressure. Shaping may be done by processes such as molding, casting, extrusion, calendaring, laminating, foaming, blowing, and many others. Nonetheless, the term plastic has a specific meaning in this context and should not be used to refer to polymers in general. The moduli as well as other properties of plastics vary widely according to their applications. For example, molding, calendaring, or extrusion of a thin film or sheet requires a material with a low modulus so that the sheet is flexible. On the other hand, manufacture of a bleach bottle demands a stiff polymer – the stiffer the better so long as it is not brittle – so that the walls can be made thinner and material saved.

The extensibility demanded in elastomers is not needed in plastics, although a degree of extensibility is important so that the work-to-break is high enough for the plastic to resist twisting and impact. Generally the properties of plastics are intermediate between those of elastomers and fibers.

Fibers, if they are going to be knitted or woven into dimensionally stable garments, require unrelenting properties. They should have high modulus and low extensibility. The fibers must be strong so that a single thread will not “pull apart,” and this requires a high modulus and molecular cohesion, properties closely related to high tensile strength and crystallinity.

It is more difficult to generalize about surface coatings and adhesives than about the other groups. A coating may require high extensibility and low modulus if it is to be applied to a soft rubber surface. On the other hand, a coating for a baked phenolic sheet may require low extensibility and high modulus. The property that both coatings and adhesives require is high adhesion, and the problem is to achieve this while maintaining a reasonable level of the diametrically opposed property of cohesion. In addition, a coating will require resistance to abrasion.

In general, coatings and adhesives tend to have low moduli, somewhere between those of elastomers and plastics. They must have some extensibility, particularly if the material is to be used on a dimensionally unstable substrate such as wood. It follows that coatings and adhesives have low crystallinity.

17.7 PLASTICS FABRICATION TECHNIQUES

Plastics are overwhelmingly the largest group of industrial polymers, and they are fabricated by a wide variety of techniques. The following is a brief review adapted with permission from *The Chemical Economy*.

Compression molding (Fig. 17.19) is practically the oldest method of fabricating plastics. It was used for the early phenol–formaldehyde resins just after World War I and is still widely used. The polymer is placed in one-half (the “female” half) of a mold and the second or “male” half compresses it to a pressure of about 1 metric ton

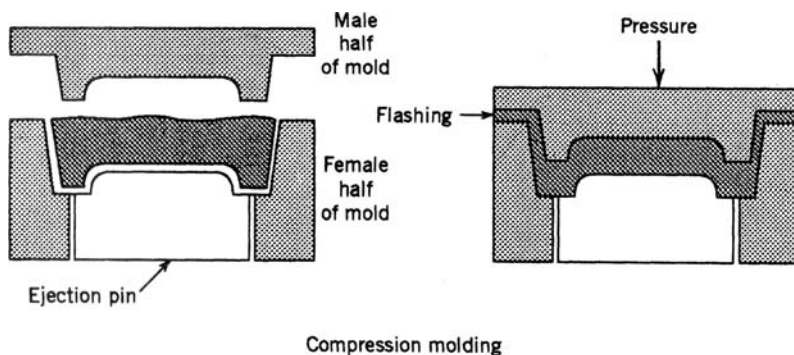


FIGURE 17.19 Compression molding.

per square inch ($1.55 \times 10^6 \text{ kg/m}^2$). The powder is simultaneously heated, which causes the resin to crosslink.

Transfer molding is a cross between compression and injection molding. It uses a closed mold, so smaller tolerances and more intricate parts can be achieved. Unlike compression molding, the resin is inserted from outside the mold and no further pressure is applied. The fixed cost of the tooling in transfer molding is greater than in compression molding, so that transfer molding is the more expensive process. The mold may contain layers of fibers or a preform.

Casting was also used before World War II. In the sheet casting of poly(methyl methacrylate), monomer is partly polymerized and the viscous liquid then poured into a cell made up of sheets of glass separated by a flexible gasket that allows the cell to contract as the casting shrinks. A simulation of high quality marble may be made using epoxy or polyester resins with powdered stone added for coloration, often with multiple colors worked in. Casting is sometimes performed under vacuum to prevent bubbles from being trapped in the cast. Casting is a slow process and is normally confined to short runs.

Injection molding (Fig. 17.20). In injection molding, the polymer is softened in a heated volume and then forced under pressure into a cooled mold where it is allowed

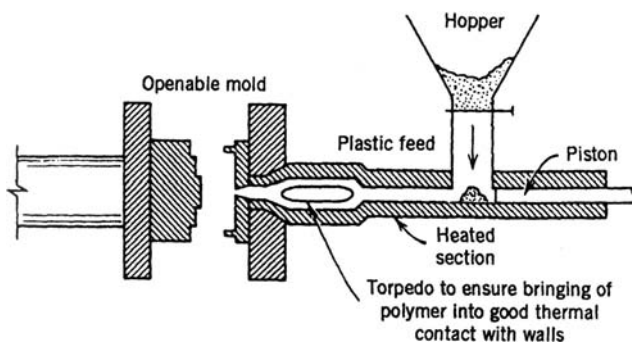


FIGURE 17.20 Injection molding.

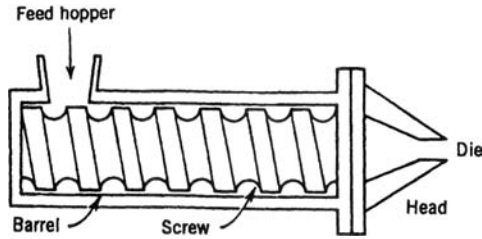


FIGURE 17.21 Extrusion.

to harden. Pressure is released; the mold is opened; the molding is expelled and the cycle is repeated. Injection molding is a versatile technique and can be used for bottle manufacture by a method identical with blow molding except that the initial “bubble” is injected rather than extruded.

A comparatively recent modification is RIM (reaction injection molding) in which thermosetting polymers are injected into the mold while plastic and allowed to cure in the mold. The widest use of the technique is with polyurethanes (Section 17.4.2). When these are used with a foam, the polymer “skins” on the cool outer wall of the mold and gives a high density outer layer with a light interior, useful in furniture.

Extrusion (Fig. 17.21) is a method of producing lengths of plastic materials of uniform cross section. The extruder is similar to a domestic mincing machine with the added facility that it can be heated or cooled. The pellets enter the screw section via the hopper, are melted, and then pass through the breaker plate into the die. The molten plastic is forced out of the die with its cross section determined by the shape of the die, but not identical with it because of stresses induced by the extrusion process. Extrusion can be used for coating electrical wiring by means of a cross-head die.

Blow molding. Blow extrusion (Fig. 17.22), in which the initial lump of polymer is formed by an extrusion process, is the commonest form of blow molding. A short length of plastic tubing is extruded through a crossed die and the end is sealed by the closing of the mold. Compressed air is passed into the tube and the “bubble” blown out

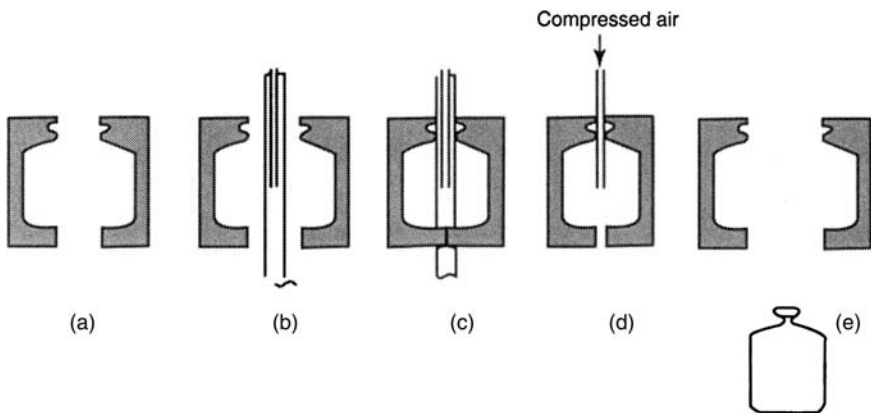


FIGURE 17.22 Blow extrusion.

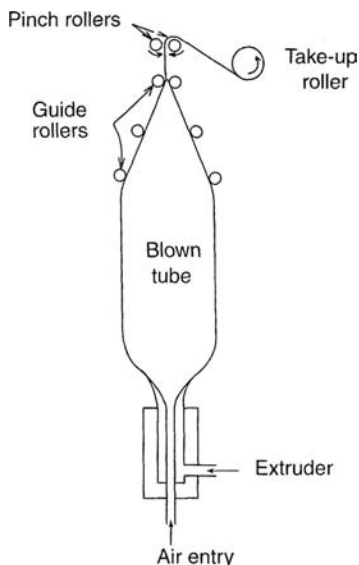


FIGURE 17.23 Production of film by extrusion and blowing.

to fill the mold. Suitable control of this process can lead to the biaxial orientation of the polymer as in poly(ethylene terephthalate) soft drink bottles.

A variation of the process is used in the manufacture of thin film (Fig. 17.23). A tube of plastic is continuously extruded and expanded by being blown to a large volume and consequently a small wall thickness. The enormous bubble of plastic is cooled by air jets and taken up onto rollers. This material can either be slit down the side to give thin film or turned into plastic bags by sealing the bottom of the tube.

Vacuum forming (Fig. 17.24) is the opposite of blow molding. A sheet of heat-softened plastic is placed over a mold and the air sucked out. The plastic is drawn down and conforms to the shape of the mold.

Calendering makes use of a preheated polymer mix that is turned into a continuous sheet by passage between two or more heated rolls that squeeze it to the appropriate thickness. If fabric or paper is fed through the final rolls, the plastic can be pressed on it

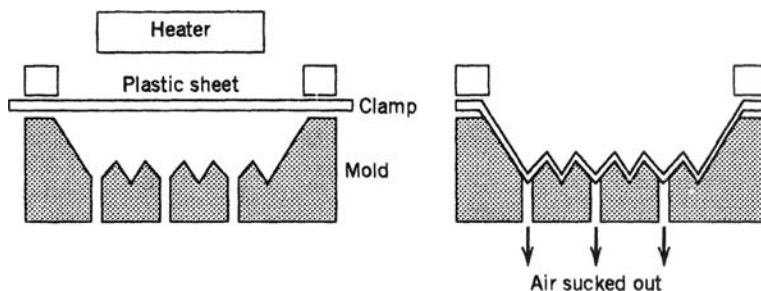


FIGURE 17.24 Vacuum forming.

to give a plastic-coated material. If the rolls are patterned, a “sculpted” appearance can be obtained.

Laminating. The best known laminates are the Formica-type decorative laminates for household use. Brown paper is impregnated with an alcoholic solution of a resole and is then cut up and arranged in piles with a suitably printed melamine–formaldehyde impregnated decorative sheet on top. Also, a photograph of wood grain may be used with a melamine–formaldehyde top coat. The whole is pressed at about 150–180°C and 3 metric tons per square inch ($4.65 \times 10^6 \text{ kg/m}^2$) to give the finished laminate.

ENDNOTES

1. The data in Figure 17.1 are guesstimates based on *Guide to the Business of Chemistry and Chem Eng. News*, 5 July 2010.
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3. A charming video about comb and brush polymers will be found at http://wn.com/comb_polymers.
4. J. Urquhart, *Chemistry World*, 7 October 2010.
5. There are a huge number of books about metallocenes. We note the very new book by G. G. Hlatky, *Olefin Polymerization by Metallocene Catalysts*, Wiley, Hoboken, NJ, 2011 and the older books by G.M. Benedikt and B.L. Goodall, *Metallocene Catalyzed Polymers*, B.F. Goodrich, Brecksville, 1998; G. M. Benedikt, *Metallocene Technology in Commercial Applications*, Noyes, Geneva, 2000; and a two-volume set, *Metallocene-Based Polyolefins*, eds. J. Scheirs and W. Kaminsky, Wiley, Hoboken, NJ, 2000.
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7. <http://www.finewoodworking.com/pages/w00060.asp>.
8. Details of the hyperbranched compound based on 1,3,5-benzenetricarboxylic acid come from www.nedo.go.jp/kiban/zairyo/eng/poly/poly005.html. See also *Chem. & Eng. News*, 6 September 1999.
9. <http://www.pharmainfo.net/reviews/dendrimer-overview>.
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11. G. Inzelt, *Conducting Polymers*, Springer, Berlin, 2008.
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17. P. Matyba et al., Graphene and mobile ions: The key to all-plastic, solution-processed light-emitting devices, *ACS Nano* **4**, 637, 2010.
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CHAPTER 18

Industrial Catalysis

Many of the organic chemicals discussed in the previous chapters were already being made before World War II. They were made by fermentation or from coal by “traditional” organic chemistry in batch processes. The advent of cheap olefinic feedstocks derived from oil and natural gas led to a switch to “hot tube” industrial organic chemistry, that is, to continuous processes that produce hundreds of thousands of metric tons of product per year. The basis for this modern organic chemistry is frequently the “appropriate” catalyst, whose exact nature is a closely guarded industrial secret.

In 1966, when catalyst theory was in its infancy, it was estimated that 70% of industrial processes involved catalysis. The percentage is now said to have reached 90%, and other sources say that 80% of today’s large scale chemical processes depend on solid, heterogeneous catalysts.¹ Catalysis was said at the turn of the century to be used in the manufacture of over \$3 trillion in goods and services. Annual royalties and fees from technology process licensing exceeded \$3.5 billion and the global merchant market for catalyst products approached \$8.5 billion. About 30% of the U. S. gross national product is generated with the help of catalysis. This chapter is therefore devoted to a brief review of catalyst technology, with emphasis on ways in which the concept of a catalyst has changed and on recent trends in the industry. We are not trying to compete with the many excellent books on academic or industrial aspects of catalysis, and our selection of topics is personal.² We shall discuss first the questions of catalyst choice and then some of the chemical engineering aspects of catalyst use. Third come the markets for catalysts and then a discussion of the different types of catalysts encountered in industry. Table 18.1 shows a summary of catalytic reactions.

18.1 CATALYST CHOICE

Unlike feedstocks and raw materials, the overriding factor for industrial catalysts is not their cost. As long as catalysts can be reused, cost is not crucial. The outstanding

TABLE 18.1 Summary of Catalytic Reactions

Class	Functions	Examples
Transition metals	Hydrogenation Dehydrogenation Hydrogenolysis (oxidation)	Fe, Ni, Pd, Pt, Ag
Semiconductors and transition metal oxides	Oxidation Dehydrogenation	NiO, ZnO, MnO ₂ , Cr ₂ O ₃ Bi ₂ O ₃ /MoO ₃ , WS ₂ , SnO ₂
Insulator oxides (main group oxides)	Desulfurization (hydrogenation) Dehydration (hydration)	Fe ₂ O ₃ Al ₂ O ₃ , SiO ₂ , MgO
Acids and acidic mixed oxides	Polymerization Isomerization Cracking Alkylation (hydrolysis) Esterification	H ₃ PO ₄ , H ₂ SO ₄ , BF ₃ , SiO ₂ /Al ₂ O ₃ , zeolites V ₂ O ₅ /Al ₂ O ₃
Bases	Polymerization (esterification)	Na/NH ₃
Transition metal complexes	Hydroformylation Polymerization Oxidation Metathesis	[Co ₂ (CO) ₈] TiCl ₄ /Al(C ₂ H ₅) ₃ CuCl ₂ /PtCl ₂ WO ₃ , WCl ₆
Dual function catalysis	Isomerization plus hydrogenation/ dehydrogenation	Pt on SiO ₂ /Al ₂ O ₃
Enzymes	Varied	Amylase, urease, proteinases
Reactions between immiscible reactants	Quaternary ammonium salts	

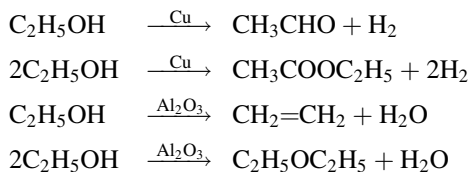
feature of modern industrial catalysts is their selectivity, that is, the extent to which they make a reaction go in a desired direction. Second, there is the access they provide to unusual “nonequilibrium” products. Third, there is the conventional role of catalysts in increasing the rate of reaction. Fourth is the problem of recovering catalysts for reuse. In choosing a catalyst, there is also the question of homogeneous versus heterogeneous catalysis. We shall discuss these in turn.

18.1.1 Reaction Velocity and Selectivity

Wijngaarden et al.² have recently defined catalysis as “the acceleration of a chemical reaction by a small quantity of a substance, which may take part in the reaction, but in the end is not changed by the reaction.” That is only part of the story. The effect of a catalyst can be so large that a quantitative difference becomes qualitative. Thus platinum catalyzes the combination of hydrogen and oxygen. In the absence of a catalyst, the reactants can apparently remain for hundreds of years without reaction.

It would appear that the platinum did not accelerate the reaction, but rather that it brought it about. The same applies to many industrial catalysts. Silver “catalyzes” the oxygen/ethylene reaction to ethylene oxide, but yield of ethylene oxide in its absence is zero.

Selectivity is crucial. A material that does not react at a measurable rate in the absence of a catalyst may react to give quite different products in the presence of different catalysts and at different temperatures and pressures. Ethanol passed over copper can give either acetaldehyde or ethyl acetate depending on conditions. Passage over alumina gives ethylene or diethyl ether.



Thus catalysis often provides a reaction route that proceeds in parallel with other existing thermal or catalytic routes. Useful catalysts cause the desired reaction to be favored overwhelmingly. Increasing the selectivity of catalysts is an important activity of development chemists. A high selectivity not only brings the financial reward of increased yield, it also reduces the problems of by-product sale or effluent disposal.

A catalyst often permits a reaction to take place at measurable speed under milder conditions than would otherwise be possible. That, in turn, may lead to a different equilibrium and a different major product. In the production of ethylene oxide (Section 5.7), no reaction would take place at 275°C in the absence of a catalyst. At a temperature at which a reaction *would* take place, only carbon dioxide and water would be formed. The silver catalyst enables the temperature to be kept sufficiently low for the ethylene oxide-forming reaction to proceed at a rate higher than the overall combustion reaction. It also means that the sequential oxidation of ethylene oxide proceeds slowly enough for the ethylene oxide to be isolated.

This is illustrated in a semiquantitative way in Figure 18.1. Ethylene and oxygen exist in a potential energy well, as shown, and there are other potential energy wells corresponding to ethylene oxide, acetaldehyde, peracetic acid, and carbon dioxide/water as indicated. The maxima are the activation energies required for the various possible catalyzed and uncatalyzed reactions.

In the absence of a catalyst, ethylene and oxygen combust directly to carbon dioxide and water. In the presence of a silver catalyst, however, the initial activation barrier is reduced and the ethylene oxide minimum becomes accessible. In the presence of a palladium catalyst, a different potential energy surface becomes accessible with acetaldehyde and peracetic acid as local minima.

The commercial development of the ethylene oxide process has concentrated on these points. The silver catalyst consists of about 15% silver as a finely divided layer on a support that acts as a heat sink to prevent undue temperature rise of the catalyst by the reaction exotherm. Furthermore, an inhibitor – several ppm of

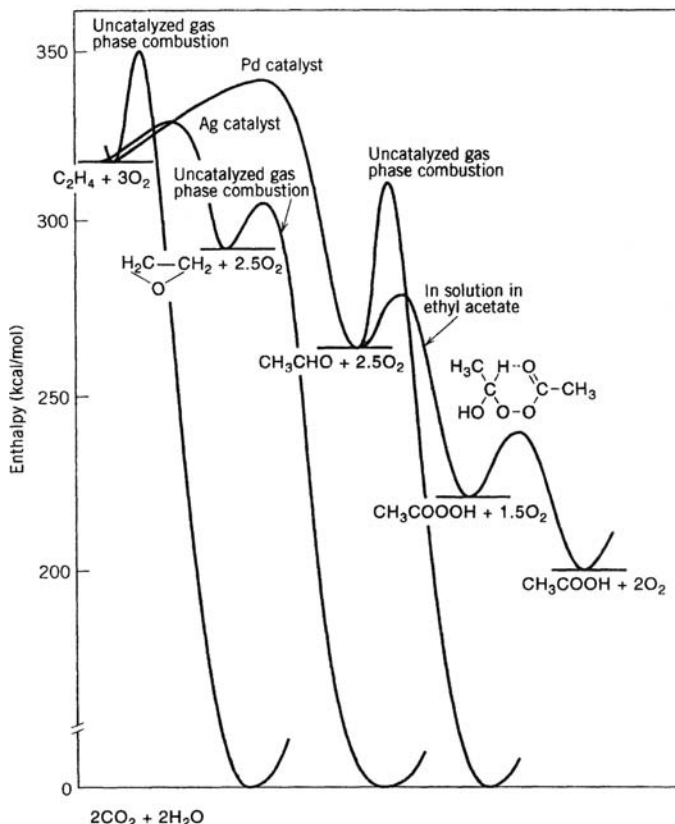


FIGURE 18.1 Potential energy diagram for the ethylene–oxygen system (based on enthalpy of $2\text{H}_2\text{O} + 2\text{CO}_2$ as zero). This figure is based on standard thermodynamic data together with activation energies from G. J. Minkoff and C. F. H. Tipper, *Chemistry of Combustion Reactions*, Butterworth, London, 1962; C. Bamford and C. F. H. Tipper, *Comprehensive Chemical Kinetics*, Vol. 5, Elsevier, Amsterdam, 1972; and K. Weissmehl and H. J. Arpe, *Industrial Organic Chemistry*, Verlag Chemie, Weinheim, 1978. The last of these claims that the peracetic acid→acetic acid reaction goes via an α -hydroxyethyl peracetate transition state formed from peracetic acid and acetaldehyde. The peracetic acid and transition state enthalpies were deduced by the methods in S. W. Benson, *Thermochemical Kinetics*, 2nd ed., Wiley, Hoboken, NJ, 1976.

dichloroethane – is often added to the system. Inhibitors are “anticatalysts.” This one decomposes to ethylene and chlorine. The chlorine adsorbs on the silver surface, influences the chemisorption of oxygen, and hence inhibits the combustion reactions.

Other measures to increase selectivity have included the promotion of the catalyst with 3.5×10^{-4} to 3×10^{-3} equivalents of potassium, rubidium, or cesium ions per kilogram of catalyst (measured as silver oxide). The effect is specific – sodium and

lithium have no effect and quantities of the active metals outside the above range do not seem to improve selectivity.

In Figure 18.1, the effect of the catalyst is always to reduce the activation enthalpy (energy) of a reaction. If the rate constant k of a reaction is represented by the Arrhenius equation $Ae^{-E/RT}$, where A is the pre-exponential factor, E the activation enthalpy (energy), R the gas constant, and T the absolute temperature, then the implication is that E is always reduced, and A remains more or less unchanged. Indeed, many textbooks state that catalysts always act in this way.

In fact, catalysts act to reduce the *free energy of activation*, so that A varies as well as E . In some examples, a catalyst raises E but also raises A by such a large amount that it still acts as a catalyst. For different catalysts of the same reaction, it often happens that a graph of $\log A$ against E gives a straight line. This phenomenon is called the compensation effect and variations in A of up to 10^{14} have been reported.³

18.1.2 Recovery of Unchanged Catalyst

If catalyst cost is to be unimportant, catalysts must be cheap or have exceptionally high activity or be recoverable in high yield. Many catalysts, especially in homogeneous reactions, cannot be recovered unchanged at the end of a reaction.

When sulfuric acid catalyzes the esterification of ethanol with acetic acid, the reaction products contain materials such as ethyl hydrogen sulfate. The sulfuric acid has also been solvated by the by-product water. This dilution reaction is highly exothermic. Because the catalyst alters the overall chemistry of the reaction, it alters the position of equilibrium and the free energy change, and fails to increase the backward and forward rates proportionately. The sulfuric acid is not present in its original form at the end of the reaction. Its recovery from the reaction products requires a further process involving expenditure of chemical energy and reversal of the hydration and sulfate-forming reactions. In practice, sulfuric acid is very cheap. In the absence of closely monitored environmental legislation, after use as an esterification catalyst, it would probably be deposited in a local river.

An example of a high activity catalyst is the fifth generation Ziegler–Natta catalyst (Section 6.2.1) for polypropylene, which produces 70,000 kg of product for only 1 kilogram of catalyst. Although the catalyst is expensive, its activity is so high that only a tiny quantity is required, and its recovery is not worthwhile. Metallocene catalysts are claimed to be even more active.

Expensive catalysts include the platinum group metals (platinum, palladium, and rhodium) used in automobile emissions control catalysts. They contribute about 75% of the cost of such catalysts. The U.S. consumption of such metals in this end use in 2010 was about 276 metric tons.^{4,5} At a typical price of \$40/g for precious metals (these prices fluctuate wildly), this amounts to about \$8.9 billion, and the recovery and recycling are worthwhile. In 2010, 24%, 21%, and 27% of platinum, palladium, and rhodium, respectively, were recovered and recycled.

18.1.3 Catalyst Deactivation

Homogeneous catalysts are obviously more difficult to recover than heterogeneous catalysts which, in principle, can simply be removed by filtration. With heterogeneous catalysts, however, the difficulty is not so much in the “recovery” part of the definition but in the “unchanged” part. Three routes to deactivation of heterogeneous catalysts are recognized – sintering, poisoning, and fouling. Sintering covers changes in surface area and structure and is irreversible. Poisoning involves chemisorption on active sites of the catalyst and is more likely to be reversible. Fouling involves physical blockage of active sites and is usually reversible.

All these processes may result from chemical reactions. Practically all industrial solid catalysts must be removed from the reactor at intervals, varying from a few months to a year, for regeneration. In the catalytic cracking of hydrocarbon fractions to gasoline (Section 4.6), a second reactor is included in the plant for continuous regeneration of catalyst, and it is only this that makes the process feasible. This is also the basis for the DuPont transport bed process for maleic anhydride production (Section 7.4.2).

In the manufacture of SNG by the Catalytic Rich Gas Process (Section 14.4), the catalyst is nickel on high surface area γ -alumina promoted with potassium. The alumina has a cubic close-packed structure. When not used as a catalyst, γ -alumina is stable up to 1100°C. In plant use, however, at a temperature as low as 400°C, it undergoes an irreversible phase change to a hexagonal close-packed structure, α -alumina or corundum. The collapse of the fine pore structure of γ -alumina and subsequent formation of corundum also leads to agglomeration of the nickel crystallites and loss of metal surface area. Hence there is a drastic reduction in catalyst activity. The lifetime of the catalyst, which cannot be recovered unchanged, is governed by the rate of sintering of alumina and nickel.

A final example is the gas phase coking of hydrocarbons at high temperatures. It is catalyzed by surfaces, especially those containing metal particles. Nickel is especially active. Electron micrographs show that the carbon deposits as spiral fibers growing from the surface and topped by a metal crystallite, which promotes further growth. The etching of the surface is thus an essential part of the catalytic process. As in the previous examples, the textbook requirement that a catalyst be recoverable “unchanged” at the end of a reaction is not strictly met.

18.1.4 Access to Nonequilibrium Products

Thermodynamicists stress the importance of equilibrium in chemical reactions. If hydrocarbons were to react to equilibrium, however, the products would be carbon and hydrogen. If sufficient oxygen were added, furthermore, the equilibrium products would be carbon dioxide and water. Most useful chemical reactions do not go fully to equilibrium. They are stopped at some local minimum in the free energy surface as in the case of ethylene oxide discussed in Section 18.1.1. Selective catalysts direct reacting systems toward these local minima.

Catalysts are said not to affect the position of equilibrium in chemical reactions but may do so in a number of ways. In the esterification reaction described in Section 18.1.2, the amount of sulfuric acid added pushes the equilibrium to the right because of its effect on the overall free energy change accompanying the reaction.

A more modern example of a catalytic system where the catalyst affects the position of equilibrium is the disproportionation of toluene (Section 10.1). The zeolite catalyst provides much greater than thermodynamic yields of *p*-xylene. The desired isomer, the *p*-xylene, is able to diffuse away from the catalytic site much more quickly than the undesired isomers. Thus, as *p*-xylene is removed, a fresh equilibrium is continually being established. This is described further in Section 18.9.

18.2 HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

Catalysts are designated homogeneous or heterogeneous depending on whether they function in a single phase or at a phase boundary. This distinction appears to have little theoretical significance. A homogeneous acid catalyst such as sulfuric acid acts in the same way as a heterogeneous acid catalyst such as silica-alumina. In certain examples of the Friedel–Crafts reaction, it is uncertain whether catalysis is homogeneous or heterogeneous. In some industrial processes, there is the possibility of operating in either mode. Meanwhile, industrial estimates are that 80% of large scale industrial processes depend on heterogeneous catalysts.

Homogeneous catalysts can be added easily to a reaction system but may be difficult to remove from the products. They are usually used in the liquid phase, although some reactants may be introduced as gases or solids. There is only a handful of homogeneous gas phase catalyzed reactions. One example is the air oxidation of sulfur dioxide to sulfur trioxide catalyzed by nitric oxide – the old lead chamber process for sulfuric acid. Another is the cracking of acetic acid to ketene at about 700°C, catalyzed by diethyl phosphate (Section 12.5.2.3).⁶

For most but not all homogeneous catalysts, the rate increase is proportional to the amount of catalyst added. Some catalytic effects saturate, and a few appear in the rate equation with a power other than one. Homogeneous catalysts are readily reproducible and give high selectivities. For this reason they are the preferred systems for academic study and have led to most of the insights we have into the mechanisms of catalytic reactions.

In heterogeneous catalysis, the mass of the catalyst is much less important than its surface area. Preparation and pretreatment of solid catalysts borders on an art, and the activity of a catalyst depends on its previous history. Catalysts achieve high surface areas because of their microporosity. Areas of 1000 m² per gram are not uncommon. Diffusion of reactants to a surface and of products away from it may present problems, as may heat transfer into or out of catalyst particles. On the other hand, heterogeneous catalysts have the great advantage of being easily recoverable. They can be used in static or fluidized beds in continuous processes. They can be used in systems where thermodynamic constraints demand high temperatures and where solution methods would therefore be impossible. They are therefore more widely used in industry.

18.2.1 Reactors for Heterogeneous Catalysts

Reactor design is dealt with in detail in chemical engineering textbooks and in dedicated treatises, and there are almost as many designs as there are reactions. One can have batch reactors, continuously stirred tank reactors (CSTRs), and plug flow tubular reactors. The first two consist of jacketed pots with inlets, outlets, and stirrers. Batch reactors are charged with the mixture of reactants plus catalyst. The reaction is allowed to proceed to as near to completion as the operator wishes; the products, unreacted starting materials, and catalyst are then separated although, as noted above, this may be difficult. Batch reactors are particularly suitable for pharmaceutical applications, where it is important to be able to trace the provenance of any component in the finished product.

In CSTRs, the reaction mixture is continuously introduced and withdrawn (Fig. 18.2a). The composition of the exiting product stream is equal to that in the bulk of the reactor. CSTRs are especially suitable for liquid–liquid reactions. The mixing of homogeneous catalysts with reactants presents few problems. In polymerization reactions, there may be difficulties if the mixture becomes viscous, but in general stirring is adequate.

It is sometimes possible to stir a heterogeneous catalyst into a liquid reaction mixture in a CSTR, but gas phase reactions occurring on solid catalysts are usually carried out in plug flow reactors, in which the reactants travel down a tube with, it is hoped, a constant residence time for any unit volume of reactants. This is, of course, unattainable, because the reactants in contact with the walls of the reactor will be stationary, but it is a desirable aim. Plug flow reactors divide into fixed and fluidized beds.

In fixed beds (Fig. 18.2b), the catalyst is compressed into pellets of approximately 1 centimeter diameter. These are packed into a single tube, and the reactants passed through it. This is called an adiabatic reactor. One drawback with it is that heat transfer within the pellets and the tube itself is poor, and the temperature variations affect the reaction. Also, there are problems with diffusion of reactants into and products out of the compressed pellets. The system is reliable, cheap, and straightforward. It works for varying flows of gases and for catalysts that are “sticky” or liable to agglomerate, but the system is applicable only to more or less thermoneutral reactions.

The above problems are reduced but not eliminated by the cooled tubular reactor (Fig. 18.2c). The catalyst pellets are packed into several long tubes, which are contained in a shell through which a heating or cooling medium can be circulated. Compared with the adiabatic fixed bed reactor, the tubes are difficult to remove and repack when the catalyst requires regeneration. The problems with heat transfer and diffusion are reduced but still remain. Even if tubes as narrow as 3 cm in diameter are used, it is still difficult to maintain a constant temperature. Active sites in the middle of catalyst pellets achieve much higher temperatures than the rest of the system. Thermal shock may even fragment the pellets leaving dust, which may block the tube. In endothermic reactions, local cooling may bring the reaction to a halt.

Fluidized beds (Fig. 18.2d) contain catalyst in small particles like grains of sand. The particles are suspended in a rapid flow of gas, which may be the reactant or an inert fluidizing gas. If the flow is accurately maintained, the bed behaves like a homogeneous

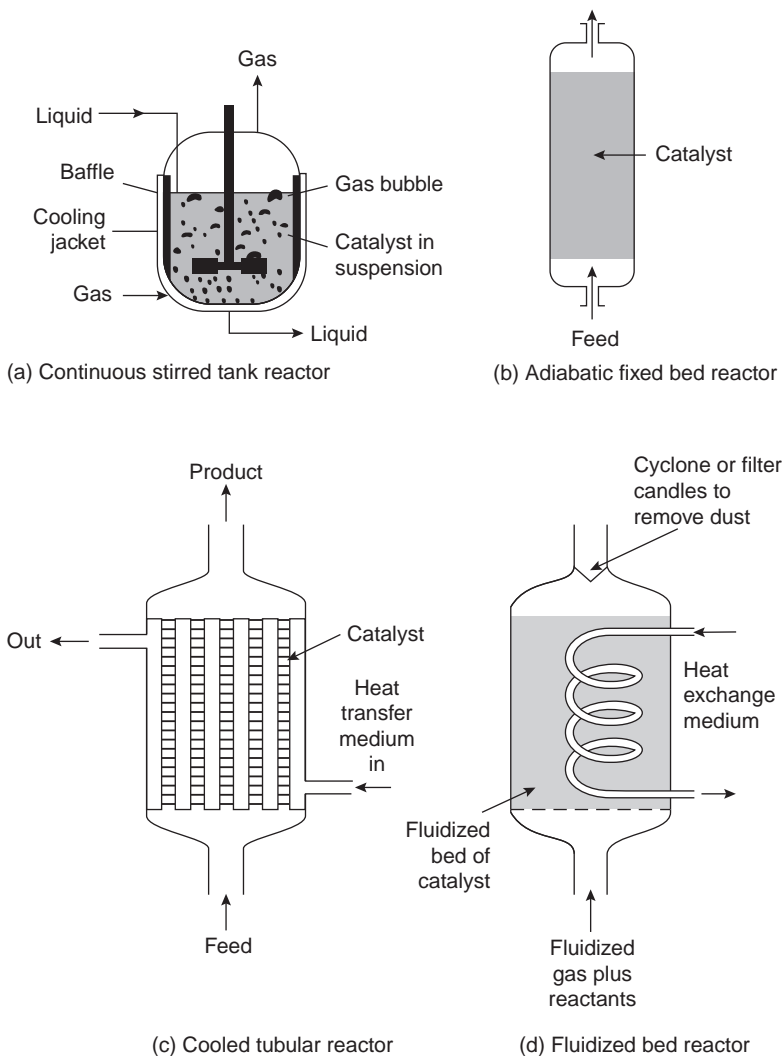


FIGURE 18.2 Reactors for catalyzed reactions.

fluid. It can be drawn off into other vessels for regeneration (Section 4.6). Heat can be added or removed by coils in the bed. Temperature equilibration is rapid. Problems of diffusion are much reduced because the catalyst particles are smaller. One drawback of the system is its intolerance to variations in gas flow. Fluidization of the bed may also be hindered by attrition, channeling, and slugging. Attrition means the wearing away of the catalyst particles as they rub against each other in the bed. A fine dust is continuously carried out of the bed and must be removed by cyclones at its exit. Channeling occurs when the gases manage to find a channel through the bed, perhaps near the wall, and travel through without adequate contact with the catalyst. Slugging is a similar

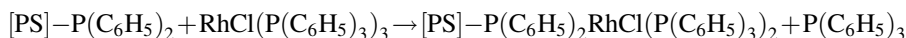
phenomenon, where the catalyst particles, agglomerating into large lumps, do not fluidize.

Fluidized beds are the more advanced technology and are used whenever the nature of the catalyst and the reaction conditions permit it. They are especially valuable when accurate control of temperature is important, as in highly exo- or endothermic reactions. The use of a fluid bed catalyst for polyethylene production by the Unipol process (Section 5.1.3) is an example, as is the use of a fluid bed for the production of acrylonitrile, which is highly exothermic (Section 6.5).

18.2.2 Immobilization of Homogeneous Catalysts

The ease of separating heterogeneous catalysts from reaction mixtures means that there is sometimes a need to turn homogeneous catalysts into heterogeneous ones. An early example is the proton-catalyzed hydration of ethylene (Section 5.9). This was originally carried out indirectly by passage of ethylene into sulfuric acid at 55–80°C and 10–35 bar, followed by hydrolysis of the ethyl hydrogen sulfate and regeneration of the sulfuric acid. In the newer process, ethylene is passed over phosphoric acid absorbed into celite—a porous diatomaceous earth that serves as a support. The lower effectiveness of phosphoric acid as a protonating agent means that more drastic conditions are required – 300°C and 70 bar – but the phosphoric acid remains physically absorbed onto the porous interior of the celite, and there is still pore space to allow access of the ethylene.

An example of the anchoring of a more sophisticated catalyst to a solid surface is the binding of the so-called Wilkinson complex (Section 18.7.2) to a polystyrene support. The polystyrene is first converted (functionalized) with a diphenylphosphine group to a polymer that may be represented as $[\text{PS}]-\text{P}(\text{Ph})_2$. This then reacts with the Wilkinson complex (chlorotris(triphenylphosphine) rhodium):



The immobilized complex preserves the ability of the Wilkinson complex to hydrogenate olefins, although the reaction may be slower.

Another example is Chiyoda's process, "Acetica," for making acetic acid. In this process, the rhodium-based methanol carbonylation catalyst is anchored to a poly(vinylpyridine) resin. This immobilization significantly simplifies catalyst recovery.

Organic polymers are not the only supports for the anchoring of catalysts. Inorganic materials are also useful. Silica is an example, and the catalyst combines with the hydroxyl groups on its surface.

Immobilization of man-made catalysts generally leads to deactivation, hence there are only a few useful examples of it. Highly active "natural" catalysts such as enzymes and complete living cells such as bacteria, on the other hand, can be attached to solid substrates without serious loss of catalytic activity. They can usefully be employed as heterogeneous catalysts. Immobilized enzymes and methods of immobilization will be discussed further in Section 18.8.

18.3 CATALYST MARKETS

The U.S. market for catalysts in 2002 was about \$10.2 billion, about 40% of the world market of approximately \$25 billion. The world merchant market for catalysts (i.e., excluding catalysts manufactured and consumed internally by industrial companies) was worth about \$10 billion and divided almost evenly between petroleum refining, petrochemicals, chemical processing, polymerization, and environmental applications (mainly automobile emissions) with a smaller contribution from fine chemicals and intermediates.⁷ This is shown in Figure 18.3. Subsequent data are fragmentary. By 2007, the merchant market had increased to \$12.2 billion and about 5.3 million metric tons, and is predicted to reach \$16.3 billion by 2012. North America was responsible for 34% of this total, Asia-Pacific for 29%, Western Europe for 23%, and other regions for the remaining 14%.⁸ Automobile catalysts made up about \$7 billion of the 2007 figure and petrochemical catalysts about \$3.1 billion. By 2010, the global market (bigger than the merchant market) for environmental chemicals had reached \$12.3 billion, energy catalysts \$4 billion, and chemicals (including fine chemicals) \$12 billion.

Furthermore, of the approximately 300 million metric tons of chemicals produced annually in the United States in the early 1990s (including inorganics), about 60% were produced with the aid of catalysts. Thus a kilogram of an average catalyst produced about 1500 kilograms of chemicals (allowing for the catalyst volume being somewhat out of date). The polypropylene example in Section 6.2.1, where 1 kilogram gives 70,000 kilograms, is exceptional for a catalyst, although typical for olefin polymerization. Catalysts are expensive and are truly specialty chemicals. They have an average cost of \$2–3 per kilogram. Even when sales figures are similar, these hide large differences in tonnage.

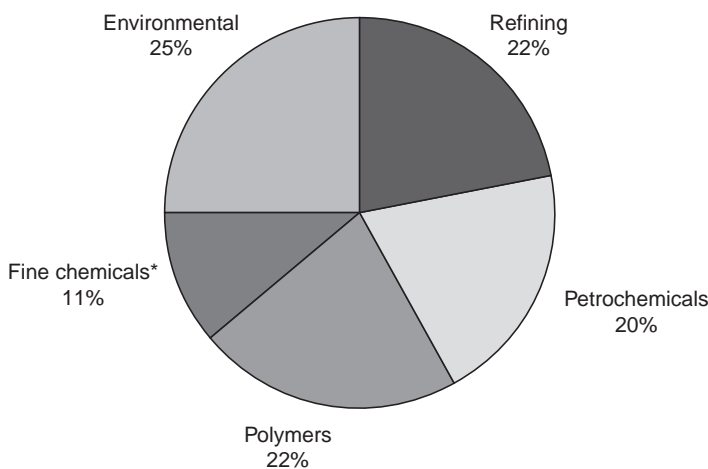


FIGURE 18.3 Global catalyst market 2002 (total = \$10.2 billion). The asterisk represents a surrogate figure that provides the merchant market for four segments. It includes intermediates and “others.”

Petroleum refining catalysts on average are the cheapest and cost about half as much per pound as chemicals catalysts. In 2008 globally, about 4 billion metric tons of crude oil was converted to petrochemicals. The three main processes responsible were hydrodesulfurization, hydrotreating (Section 4.11), and fluid catalytic cracking.

They converted 2 billion and 700 million metric tons, respectively, of petroleum to transportation fuel and valuable petrochemicals, making them the world's number one and two most important catalytic processes.⁹ According to BASF, refinery catalysts accounted in 2008 for \$3.9 billion of the overall \$14.1 billion market for heterogeneous catalysts, behind emission control (\$6.2 billion) and chemistry (\$4.1 billion) catalysts.

Cheap acid catalysts used for alkylation account for 90% by weight but only about 32% by value in the refinery sector. The new solid acid catalysts are more expensive, as are the high activity zeolite catalysts for catalytic cracking. The other petroleum refining catalysts – for hydrocracking, reforming, and isomerization – are of less significance, but hydrotreating received a boost in 2005/2006 with the implementation of low sulfur legislation in the United States and is now of major significance.

Figure 18.4 shows the global market for polymerization catalysts in 2002. It had expanded by 2010 because of the growth of polymer capacity in the Middle East/Africa and Asia-Pacific. There is unfortunately a problem of definition. Materials that promote polymerization may be divided into true catalysts such as metal complexes, metal oxides, and anionic and cationic catalysts (Chapter 17) and initiators, which appear as end groups in the final polymer. Although the formal equations depicting the polymerization reactions are similar, compounds that appear in the final product differ fundamentally from those that are regenerated and can in principle be separated and reused. Nonetheless, this distinction is not always recognized in the commercial

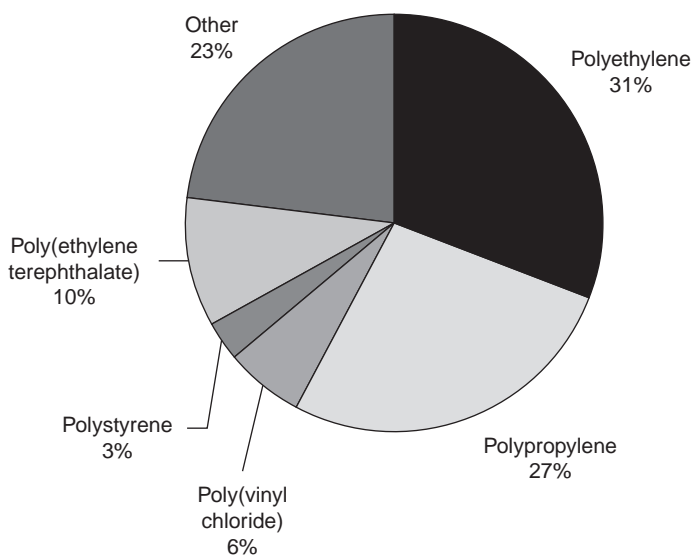


FIGURE 18.4 Global market for polymerization catalysts, 2002 (total = \$20.5 million).

world, and the figure given above is inflated by the inclusion of free radical initiators. The most expensive polymerization catalysts are the single site metallocene catalysts, although their price has been dropping as they become more widely used. Ziegler catalysts used for polypropylene and polyethylene, and the dibutyl tin and triethylenediamine (DABCO or diazabicyclooctane), for polyurethanes are also expensive.

The main group in the chemicals category is general organic synthesis. It includes a variety of catalysts for esterification, hydrolysis, alkylation (cumene and ethylbenzene dominate), and halogenation.

Oxidation catalysts are a special class, and about half this market by value is the silver catalyst used to make ethylene oxide. In terms of tonnage, the relatively cheap catalysts for the oxychlorination of ethylene (Section 5.4) make up about a third by weight but only about 5% by value. Another expensive oxidation catalyst is the manganese and cobalt salts in acetic acid plus bromine promoter for oxidation of *p*-toluic acid to terephthalic acid (Section 11.3.1). Palladium on charcoal is also used in this process to catalyze hydrogenolysis of by-product 4-carboxybenzaldehyde to *p*-toluic acid (Section 11.3.1). Added together, these produce a process that is expensive in terms of catalyst. Further cost is added by the decomposition of the acetic acid, only part of which can be recovered for reuse.

The final category of chemical synthesis catalysts is the iron-based catalysts for ammonia, and chromium-based catalysts for methanol from synthesis gas. The cost is relatively low, but the tonnage for ammonia alone is about a fifth of total catalysts for chemicals.

Apart from the *p*-toluic acid catalyst mentioned above, the main hydrogenation catalysts are:

- Raney nickel for margarine and related processes
- Nickel and to a lesser extent palladium or platinum on lithium oxide for hydrogenation of benzene to cyclohexane
- Silver gauze for dehydrogenation or oxidative dehydrogenation of methanol to formaldehyde
- Cobalt and rhodium catalysts for the oxo process

The main dehydrogenation process is the conversion of ethylbenzene to styrene.

The fine chemicals and intermediates category embraces the catalysts used by the pharmaceuticals, agrochemicals, and flavors and fragrances industries. It is fragmented, if only because of the number of chemicals produced, and depends to a greater extent than the heavy chemicals industry on the catalysts that would be found in an academic chemistry laboratory.

The catalysts for automobile emission control are based on platinum group metals – platinum, palladium, rhodium, ruthenium, and iridium. These are almost an order of magnitude more expensive than other chemicals catalysts, and the tonnage is correspondingly smaller. The U.S. consumption of platinum group metals in 2010 for use in catalysts was 325 metric tons, up from 243 metric tons in 1998. Forty percent of total platinum demand was for auto catalysts and only 30% for jewelry, compared

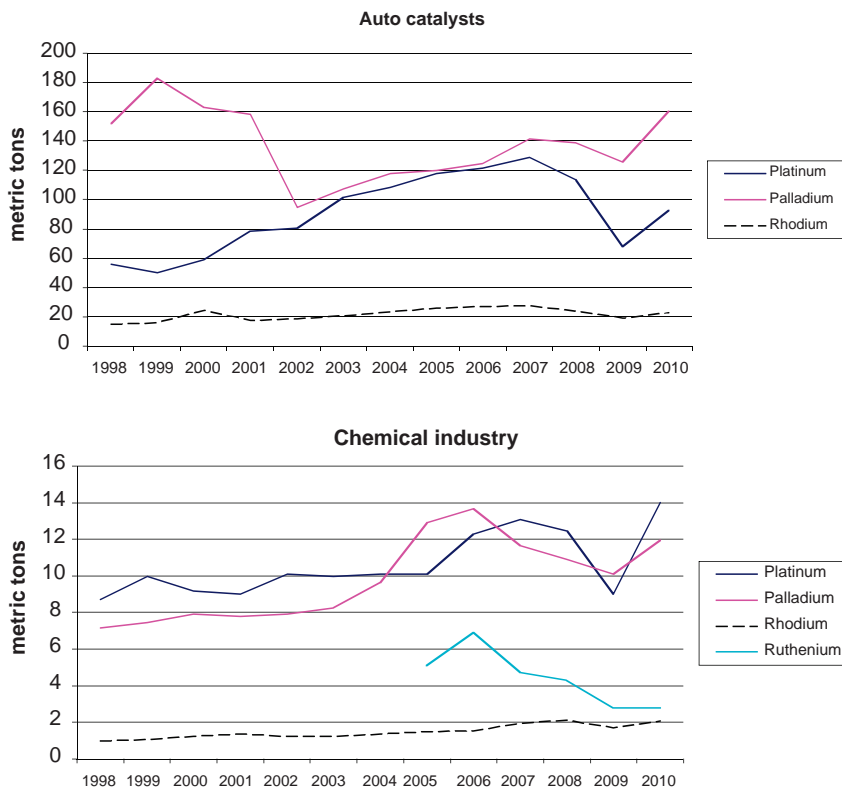


FIGURE 18.5 Platinum group metals as catalysts.

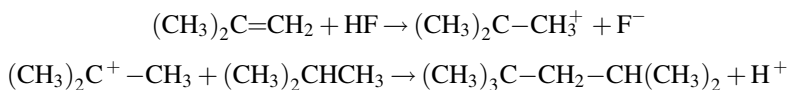
with 33% for auto catalysts and 45% for jewelry in 1998. A mere 5.6% went into chemicals and 2.9% into petroleum refining. Almost a quarter of demand was satisfied by recycled material. Demand is volatile and the figures over a ten-year period are shown in Figure 18.5. Note that platinum group statistics are given in troy ounces; 1000 troy ounces equals 31.3 kg. Automobile sales are particularly significant in influencing the market.^{10,11}

Thus the auto catalyst market is dominated by platinum group metals, but the petroleum and chemicals markets are dominated in terms of tonnage by simple acidic or metal oxide catalysts. Nonetheless, there is a range of relatively modern high technology catalysts, which repay their higher prices. They are often sold together with “know-how” and are steadily improved. Examples are the zeolites, and the catalysts for ethylene oxide production and Ziegler polymerization.

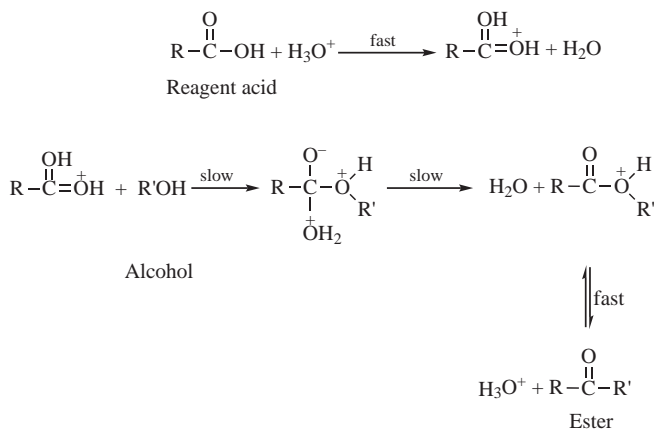
Environmental applications are seen as the growth market for catalysts in the developed world, while petroleum refining catalysts are expected to be static. Figure 18.3 shows environmental catalysts as 25% of the global market, but the figure for the United States, where there is extensive environmental legislation, is as high as 30%. Growth is also expected in developing countries in catalysts for synthesis-gas-to-chemicals, refinery processes, and polymerization.¹²

18.4 CATALYSIS BY ACIDS AND BASES

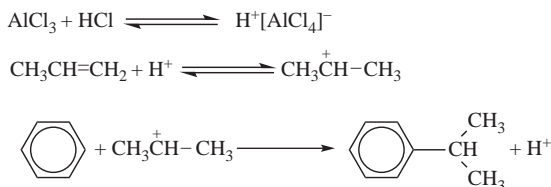
Acid catalysis is the most widely used form of catalysis in the chemical and refining industries. Alkylation (Section 4.10) is brought about by cheap acidic catalysts. Sulfuric acid was used in the past, but hydrogen fluoride has replaced it in most modern refineries. The mechanism is a typical acid catalysis in which the catalyst donates a proton to the reactant to give an ion, in this case a carbocation that reacts as shown below for the alkylation of isobutane by butene:



Sulfuric acid is also the usual catalyst in esterification reactions, which proceed by a similar mechanism:



Brønsted and Lewis acids also act as catalysts by proton donation. HCl/AlCl_3 catalyzes the Friedel–Crafts reaction between benzene and propylene by the following mechanism, which has been confirmed by isotopic labeling.



Catalytic cracking (Section 4.6) resembles alkylation and provides another example of acid catalysis. It differs in that a solid surface provides the acidity, and it acts either by willingness to accept an electron pair from another species (Lewis acid) or to donate a proton (Brønsted acid). The original catalytic cracking catalyst was silica-alumina, developed by Houdry in the 1930s. The modern catalyst is the rare earth form of a zeolite structure, and it largely suppresses the reactions leading to the excessively volatile C_3 – C_4 products.

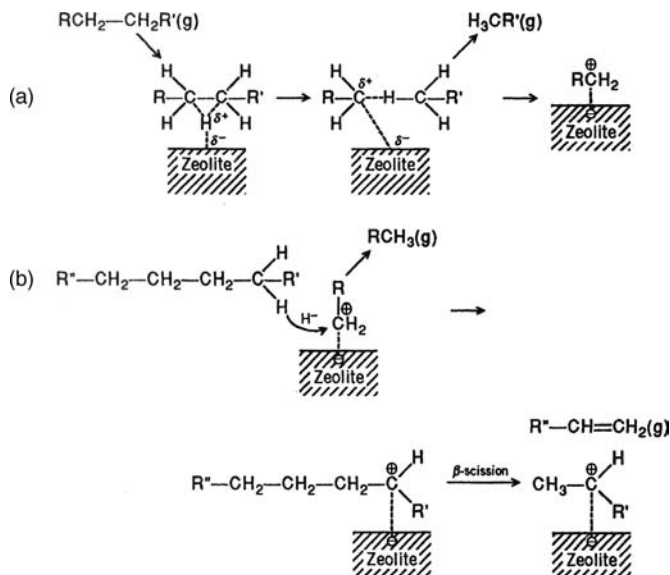
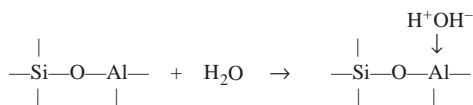


FIGURE 18.6 Scheme postulated for the mechanism of alkane cracking on acidic zeolite catalysts. (a) Protolytic route to formation of chemisorbed carbenium ion via cracking of larger alkane (RCH_2-CH_2R'). (b) Route for replacement of carbenium ion via hydride transfer from a gas phase alkane ($R''-CH_2-CH_2-CH_2-CH_2-R'$), showing the β -scission process leading to the release of an alkene ($R''-CH=CH_2$) to the gas phase. After a scheme given by A. Corma, J. Planelles, J. Sáúchez-Marin, and F. Tomás *J. Catal.* **93**, 30 (1985). Reproduced with permission from *Catalysis at Surfaces*, I. M. Campbell, Chapman and Hall, 1988.

Zeolites are aluminosilicates and are the basis for shape-selective catalysis (Section 18.9). Their structure is dominated by the fourfold coordination of silicon, each atom being bonded to four tetrahedrally arranged oxygen atoms. Substitution of a silicon atom in such a structure by aluminum, with its valency of three, leaves a vacant tetrahedral position in the lattice where a pair of electrons can readily be accepted to complete the valency octet. Thus the species can function as a Lewis acid. Alternatively, interaction with water can lead to a Brønsted acid site with an available proton:



The cracking of a larger to a smaller alkane on such an acid site may be represented as in Figure 18.6.

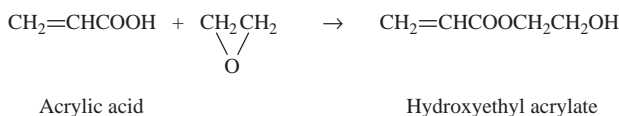
The zeolite catalyzed alkylation of benzene with ethylene and propylene to give ethylbenzene and cumene, respectively, is a specific example of the trend toward solid acid catalysts in the chemical industry. A further example is UOP's Detal process for making linear alkylbenzene (LAB). In this process, mono-olefins, both α -olefins and

those with internal double bonds, are reacted with benzene over a solid acid catalyst believed to be a fluorided silica-alumina.

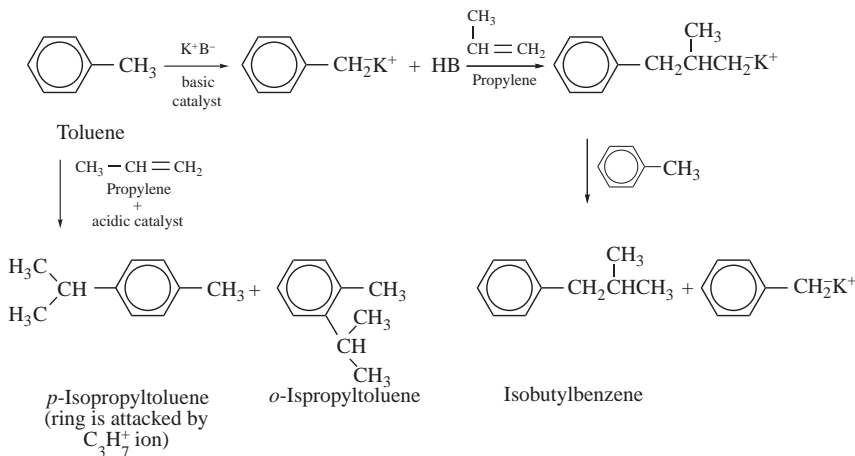
The production of bisphenol A by the reaction of acetone and two equivalents of phenol was historically carried out using mineral acids such as HCl. Modern plants have now switched to solid catalysts composed of cationic ion exchange resins. In all of these units, the use of solid catalysts simplifies the plant layout and obviates the need to handle and dispose of the noxious liquid acid catalysts.

Catalysts for catalytic cracking provide the most valuable market in the field of petroleum refining. They have to be tailored to meet changing demands for the balance and specification of products. In the past, gasoline was required to meet only a few specifications; now it must meet strict composition standards. In the past, catalytic cracking produced 30–35% of the gasoline pool. Now it is seen as a source of feedstocks for other applications such as increased yields of C₄ and C₅ olefins for the production of octane-building oxygenates and alkylates, as well as propylene for the chemical industry.

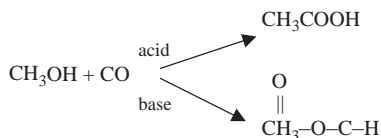
Basic catalysis is rarer in industry than acidic catalysis. Examples include one-shot phenol-formaldehyde resins (Section 17.4.1) and isocyanate formation. The opening of an epoxide ring frequently depends on a basic catalyst. An example is the reaction of ethylene oxide with acrylic acid to give hydroxyethyl acrylate, a trifunctional monomer used in baking enamels. The catalyst is a tertiary amine or quaternary ammonium salt.



Whether a catalyst is acidic or basic can alter the reaction products. Alkylation of toluene with propylene in the presence of a Friedel–Crafts (acidic) catalyst leads to ring alkylation to give *o*- and *p*-isopropyltoluene. A potassium catalyst, however, promotes alkylation of the methyl group to give isobutylbenzene, an intermediate for the manufacture of the nonsteroidal anti-inflammatory agent ibuprofen.



Similarly, methanol and carbon monoxide give acetic acid in the presence of an acid catalyst and methyl formate in the presence of a base.



18.5 DUAL FUNCTION CATALYSIS

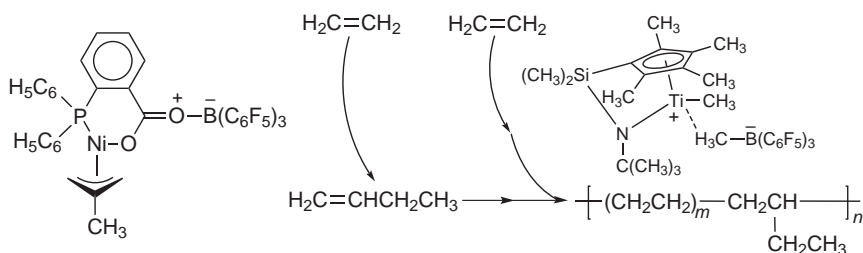
Catalytic reforming (“platforming,” Section 4.8) is brought about by a dual function catalyst, a mixture of two catalysts, each of which performs differently. Reforming catalysts are based on a mixture of an acidic isomerization catalyst ($\text{SiO}_2/\text{Al}_2\text{O}_3$) with a hydrogenation/dehydrogenation catalyst (Pt). The modern form is a platinum–rhenium alloy supported on alumina with sufficient sulfur added partially to poison the metal surface. The combined action of rhenium and sulfur inhibits coking. The Israelis are reported to be experimenting with a soluble rhodium catalyst inside a porous matrix of silver atoms.¹³

Typical feedstocks are cyclohexane and methylcyclopentane. A dehydrogenation catalyst can convert cyclohexane to cyclohexene and then to benzene, and an acidic catalyst can convert methylcyclopentene to cyclohexene. Only a dual function catalyst can convert methylcyclopentane to benzene. For this transformation, the two types of catalytic sites are required with transfer of an olefinic intermediate between the sites. The same effect could not in many cases be achieved by successive beds of the two catalysts. In a reaction of the type, $\text{A} \rightleftharpoons \text{B} \rightarrow \text{C}$, in which the equilibrium of the first reaction lies to the left, two beds of single function catalyst would not bring about reaction because not much of B would be formed in the first bed. On a dual function catalyst, however, the small quantity of B is removed as soon as it is formed. More A consequently changes to B, and the reaction to give C is accomplished. The distances between the different catalytic sites govern the effectiveness of a dual function catalyst. *n*-Heptane will reform over a mixture of catalysts of particle size 1.0–10 μm but not 100–1000 μm .

Hydrotreating catalysts are cobalt/molybdenum or nickel/molybdenum on alumina or possibly silica. These are typical hydrogenation/dehydrogenation catalysts based on transition metals. Hydrocracking catalysts are palladium or nickel–tungsten on zeolites.¹⁴ Increasingly strict regulations on sulfur content of refinery products mean that there is pressure on catalyst producers to upgrade their products. There was the possibility of a move from transition metals to the more expensive but more efficient noble metal catalysts, but this seems to have been abandoned.

A recent example of dual function catalysis is provided by a process that produces polyethylene copolymers directly from ethylene. The catalyst system consists of a nickel–borane adduct based on tris(pentafluorophenyl)boron, which catalyzes the dimerization of ethylene to 1-butene, and a commercial organotitanium catalyst for polyethylene modified to include borane functionality that copolymerizes the ethylene with the 1-butene. The extent of branching in the product depends on the nickel–titanium ratio. The advantage of such a process is that it provides a linear low

density polyethylene (Section 5.1.4) without the added cost of an α -olefin component such as 1-hexene. Its drawback is that it is complicated, and this is presumably the reason why it has not yet been commercialized.



18.6 CATALYSIS BY METALS, SEMICONDUCTORS, AND INSULATORS

The majority of heterogeneous catalysts are metals and metal oxides. Pure metals are rarely used in industrial processes, except for silver for ethylene oxide, and noble metals for hydrogenation/dehydrogenation and hydrogenolysis.

Metals and metal oxides may alternatively be classified as *p*- and *n*-type semiconductors and insulators. At the surfaces of these materials, reactants can adsorb. Physical adsorption is weak ($\Delta H \approx -40$ kJ/mol) and does not lead to catalytic activity. Chemisorption (dissociative adsorption) on the other hand is strong ($\Delta H \approx -400$ kJ/mol) and the adsorbents themselves dissociate and form chemical bonds with the surface.

In the Haber process, for example, the reactants both adsorb and dissociate on iron. Hydrogen dissociates freely even at liquid air temperatures, but nitrogen does not do so until about 450°C, and this is the rate-determining step. Once the nitrogen molecules have dissociated (with adsorbed atoms written $\text{Cat} \equiv \text{N}$, where Cat is the catalyst) the atoms can react readily with neighboring hydrogen atoms to give $\text{Cat}=\text{NH}$, $\text{Cat}-\text{NH}_2$, and finally $\text{Cat} \cdots \text{NH}_3$ from which the NH_3 is easily desorbed.

Table 18.2 lists the heats of adsorption of nitrogen on various surfaces. On glass and aluminum only physical adsorption occurs, and these materials do not catalyze ammonia production. Iron, tungsten, and tantalum all give dissociative adsorption, but the preferred catalyst is iron because it has the smallest heat of adsorption, and therefore the products are most easily desorbed.

The theory of catalysis by way of chemisorption provides a reasonable explanation for catalysis by metals. The mode of action of “pure” metal oxides and

TABLE 18.2 Heats of Adsorption of Nitrogen on Various Surfaces

Surface	ΔH (kJ/mol)
Glass	~ -7
Aluminum	~ -42
Iron	~ -293
Tungsten	~ -397
Tantalum	~ -585

nonstoichiometric metal oxides is more complicated, and an explanation had to await a quantum mechanical theory of solids and the application of this to heterogeneous catalysts. Together with the crystal and molecular orbital ligand field theories, these now provide substantial theoretical underpinning for the catalytic effects of semiconducting metal oxides.

The large majority of catalytically active metals belong to the transition series. Consequently, it appears that catalytic activity is related to the state of the d bands, corresponding to the assembly of d orbitals at the catalyst surface. The crystal surface of a semiconductor may be thought of as having a supply of electrons and a supply of “holes,” where electrons can locate themselves. These either donate electrons to adsorbed molecules or draw them out. Thus they participate in reactions as free valences, so that the addition of a heterogeneous catalyst to a reactant system is in some ways like the addition of free radicals. In general, oxidation reactions are catalyzed by *p*-type semiconductors that have surplus “holes,” whereas hydrogenations are brought about by *n*-type semiconductors that have excess electrons. This fits in with a definition of oxidations as reactions in which electrons are lost and reductions as reactions in which they are gained. Insulators are effective for dehydration.

Another way of looking at this is to think of catalysts as weakening chemical bonds either by feeding electrons into antibonding orbitals on adsorbed molecules or by withdrawing them from bonding orbitals.

The theory of heterogeneous catalysis by semiconductors is complicated and is still developing. Fundamental knowledge about the mechanism of heterogeneous catalysis may make it possible one day to tailor-make a catalyst that functions as efficiently and selectively as the semiconductor devices used in modern electronics. It may also be possible to minimize problems of catalyst poisoning either by modification of catalyst structure or by the admixture of antidotes to the feedstock or intermittently to the catalyst.

18.6.1 Catalysts for Automobile Emission Control

As is evident from Figure 18.5, the most widespread application of precious metal catalysts is in automobile emission control. The exhaust gases from an internal combustion engine running on unleaded gasoline contain nitrogen, water, oxygen, and carbon dioxide, all of which are harmless, if one discounts the possible contribution of carbon dioxide to the greenhouse effect. They also contain unburned and cracked hydrocarbons, carbon monoxide, and oxides of nitrogen NO and NO₂ (known together as NO_x.) These are the major pollutants.

A catalytic converter must oxidize the hydrocarbons and the carbon monoxide while reducing the NO_x to nitrogen. It must perform at a low temperature, because unburned hydrocarbons are worst during start-up, but it must also operate as high as 600–700°C. Contact times are likely to be between 100 and 400 milliseconds, so efficient catalysis is essential. To ensure adequate contact between gases and catalyst, the catalyst is supported on a monolith with narrow channels.

The demands on the catalyst are so severe that the base metals proved inadequate and noble metals on alumina supports must be used. At one point, it was thought that a

Similar intermediates are probably involved in the Halcon/Eastman route to acetic anhydride.

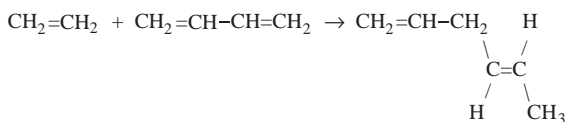
The DuPont synthesis of adiponitrile from butadiene and hydrocyanic acid (Section 7.1.5) involves a coordination catalyst with a ligand to give anti-Markovnikov addition.

Coordination catalysis is usually performed homogeneously in solution but sometimes there is a choice. In the metathesis of olefins, for example (Section 4.14), WO_3 will act as a heterogeneous catalyst, whereas WO_3 plus $\text{C}_2\text{H}_5\text{AlCl}_2$ in ethanol will work in solution. Similarly, in the Wacker process for vinyl acetate (Section 5.5), the mechanism was worked out for the homogeneous liquid phase reaction, but the system proved too corrosive, and the workable industrial process finally involved a gas phase reaction with a heterogeneous catalyst.

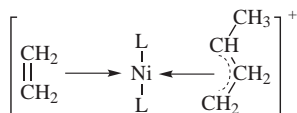
18.7.1 Catalysts for Stereoregular Compounds

Coordination catalysis can lead to stereoregular and regioselective products. An example is Ziegler–Natta catalysis, which gives stereoregular polymers (Section 5.1.1). A further example is *trans*-1,4-hexadiene, which is used as the diene in ethylene–propylene–diene monomer elastomers (Section 5.2.5). *trans*-1,4-Hexadiene has been made from ethylene and butadiene by DuPont since 1963 and has the distinction of being the first chemical to be made by a rhodium-catalyzed process. The U.S. production is approximately 10,000 metric tons/year.

The catalyst is a dilute solution of rhodium chloride in ethanolic hydrogen chloride, which gives $\text{RhCl}_3(\text{H}_2\text{O})_n$. This rhodium compound is reduced to a rhodium(I) complex, which may be in equilibrium with a rhodium(III) hydride. Ethylene and butadiene are passed into the mixture. Butadiene reacts with the rhodium complex to give an π -crotyl complex that, in turn, couples with ethylene to give *trans*-1,4-hexadiene:



Ziegler catalysts based on nickel, cobalt, and iron salts also bring about the reaction. Cobalt and iron give the *cis* isomer while nickel gives the industrially important *trans* isomer. The butadiene–nickel–ligand–ethylene complex has the approximate structure



in which the two hydrocarbons are bonded to the nickel atom, as ligands, through their double bonds.

A third example is the synthesis of β -formylcrotyl acetate, shown in Figure 18.7. β -Formylcrotyl acetate (**I**) is an important intermediate in the synthesis of vitamin A.¹⁵ Its precursor is 1,4-diacetoxy-2-butene (**II**). The precursor is made as a *cis-trans* mixture from acetylene and formaldehyde via butynediol (**III**) and butenediol (**IV**) or, in a newer process, from butadiene (**V**) and acetic acid (**VI**). The latter process also gives 1,2-diacetoxy-3-butene (Section 12.3.1).

Two routes to β -formylcrotyl acetate have been developed. In the BASF process, the mixture of diacetoxybutenes is heated with platinum (**IV**) chloride in a stream of oxygen and chlorine. The lowest-boiling isomer (**VII**) distills out in high yield and is hydroformylated with a rhodium catalyst. Usually, in such reactions, a ligand is added to give a linear aldehyde but, in this case, it is omitted and the desired branched product (**VIII**) predominates in the mixture of products (**VIII**) and (**IX**). Also, the rhodium, unlike cobalt, does not promote the migration of the double bond that would be required for the formation of a linear product.

Treatment with sodium acetate in acetic acid selectively eliminates acetic acid from the branched product to give the desired β -formylcrotyl acetate.

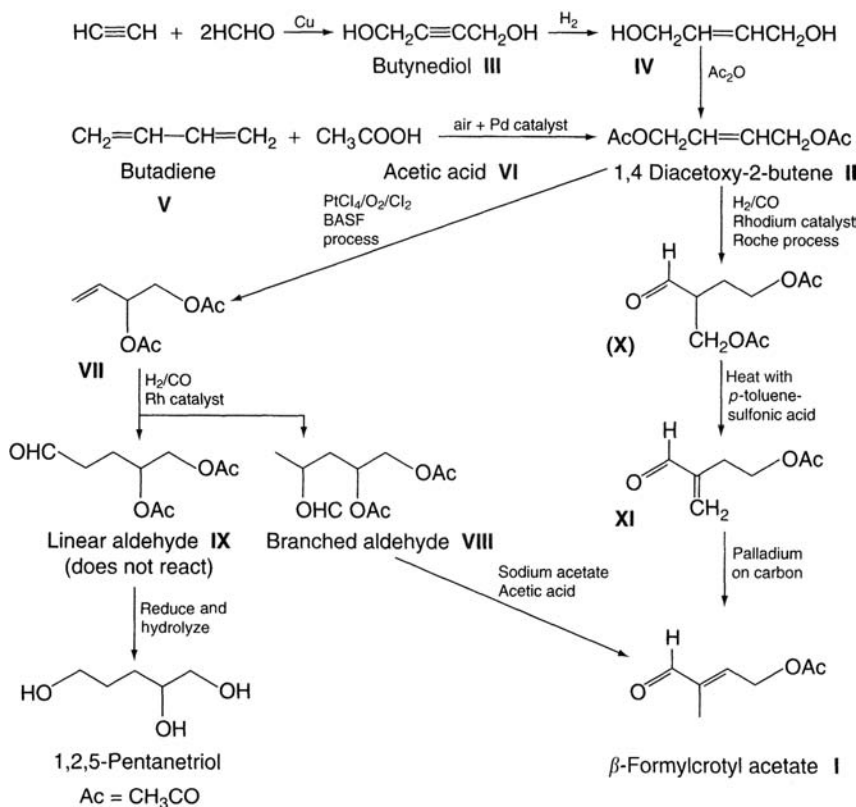


FIGURE 18.7 Synthesis of β -formylcrotyl acetate.

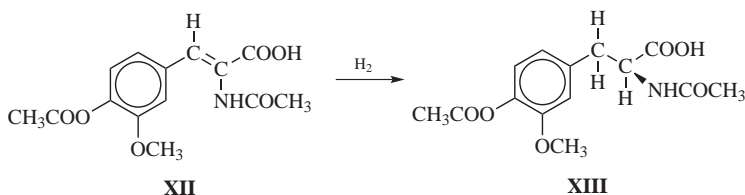
The linear aldehyde does not react and is separated, reduced, and hydrolyzed to 1,2,5-pentanetriol, used as an intermediate in the manufacture of synthetic lubricants.

The Roche process uses rhodium in a different way. It starts with the isomer (**II**) in Figure 18.7, which is hydroformylated with a conventional catalyst $\text{RhH(CO)[P(C}_6\text{H}_5)_3]_3$ that has been pretreated with sodium borohydride. Because the original double bond was internal, the aldehyde that results is still branched but has the structure (**X**). Heating with *p*-toluenesulfonic acid selectively eliminates acetic acid to give (**XI**), and palladium on carbon isomerizes the double bond to β -formylcrotyl acetate.

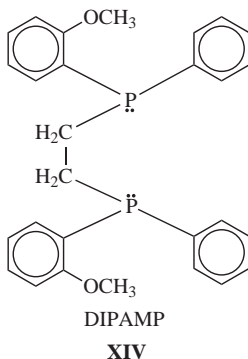
The latest catalysts for stereoregular polymer synthesis are the metallocenes, and they are discussed in Section 17.3.12.

18.7.2 Asymmetric Synthesis

Monsanto's asymmetric synthesis of levodopa¹⁶ was a landmark not only in industrial chemistry but in organic chemistry generally. The key step was the hydrogenation of the olefin (**XII**) to a specific optical isomer of dihydroxyphenylalanine (**XIII**):



The hydrogenation was carried out in the presence of a soluble rhodium catalyst bearing a chelating biphosphine ligand, DIPAMP:



The ligand is itself asymmetric and creates an unsymmetrical environment about the rhodium atom that leads to selective hydrogenation on the back face of the $\text{C}=\text{C}$ bond.

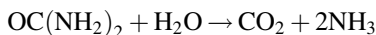
Most of the early stereospecific syntheses involved hydrogenation. Different stereospecific catalysts turned out to be valuable in different hydrogenations. The Wilkinson catalyst $\text{RhCl}[\text{P}(\text{C}_6\text{H}_5)_3]_3$ is selective for unhindered $\text{C}=\text{C}$ double bonds and causes little isomerization in the substrate, that is, the organic reagent. The catalyst $[\text{Ir}(\text{cod})(\text{PCy}_3)\text{py}]^+$ is active for very hindered $\text{C}=\text{C}$ groups and, if a functional group such as $-\text{OH}$ is present in the olefin, the catalyst will bind to it and then add hydrogen to the double bond. [The symbols (cod), (PCy_3) , and py, respectively, represent the ligands cycloocta-1,5-diene, tricyclohexylphosphine, and pyridine.]

In addition to hydrogenation, a reaction of potential importance is stereoselective epoxidation, which adds an oxygen atom to one face of an olefinic double bond. The olefin is treated with *t*-butyl hydroperoxide in the presence of a titanium complex of diethyl tartrate. The (+) and (−) tartrate isomers produce different optical isomers of the epoxide. For example, allyl alcohol reacts to give either (2*R*) or (2*S*)-glycidol. Either isomer can be reacted with 1-naphthol to give an epoxide which, with isopropylamine, gives the active (2*S*) form of the antiangina drug propranolol. The naphthol is so large, it sterically prevents *R*-formation.

Chiral syntheses are increasingly important in the pharmaceutical and fine chemical industries. In May 1992 the FDA “strongly urged companies to evaluate racemates and enantiomers for new drugs” and, by 2000, 35% of drug sales were single isomers, up from 7% in 1985. According to a recent book, chiral drugs in an optically pure form are now present in 68% of the top 200 brand-name drugs, and in 62.5% of the top 200 generic drugs.¹⁷ Chiral synthesis is and will be of much less importance in the bulk organic chemicals industry.

18.8 ENZYMES

Enzymes are the oldest industrial catalysts. In certain respects they are also among the newest. Enzymes are biological catalysts, and many show high specificity. For example, urease will only catalyze urea hydrolysis:



Some enzymes will attack certain chemical groups wherever they occur (group specificity). For example, proteolytic enzymes will split the peptide linkage. Proteolytic enzymes will only attack peptides made up either from L-amino acids or from D-amino acids, and this is called stereochemical specificity.

Enzymes are proteins but may be associated with nonproteins (cofactors) essential to their activity. Cofactors may either be simple metal ions like Zn^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , or Cu^{2+} , or organic molecules. In the latter case they are called coenzymes or prosthetic groups. Enzyme activity is usually related to a small region of the molecule referred to as the active center. At low concentrations of substrate, the rate of enzyme action is directly proportional to both enzyme and substrate concentration. If the concentration of substrate is raised, however, the rate ceases to increase and becomes

independent of substrate concentration. Thus enzymes are only efficient in dilute solution. Furthermore, they operate only under a limited range of pH (rarely < 4) and temperatures (usually $< 50^{\circ}\text{C}$), and reactions become very slow as 0°C is approached. Nonetheless, molecule for molecule, enzymes are much more effective than non-biological catalysts.

The mechanism of their action varies widely. The push–pull mechanism of acid–base catalysis is one route. The enzyme forms a complex with a molecule of reactant. The latter is bound to two active sites on the enzyme molecule and one of these “pushes” electrons while the other “pulls” them, to give a concerted action. Another mechanism is transition state compression to facilitate simultaneous bondmaking and breaking. Hydrogen bonding stabilizes intermediates.

Enzymes are used in isolated applications such as the addition of proteolytic enzymes to detergents. Fermentation is, of course, based on enzymes (Section 16.6). Although that was an important route to chemicals between World Wars I and II, enzymes as opposed to fermentation have not recently found application in large tonnage chemical production except for ethanol for fuel, high-fructose syrups (Section 16.1), and 6-aminopenicillanic acid. These and various lower tonnage enzyme processes are discussed in Section 16.5.

One problem of enzyme technology was solved when it was realized that enzymes retain their activity when attached to an insoluble matrix by a chemical linking agent. Such enzymes are described as immobilized. There is continuing interest in immobilized enzyme processes because, unlike fermentation processes, they do not use whole cells that require separation from reaction batches. They can be treated more like conventional heterogeneous catalysts and can work in continuous processes.

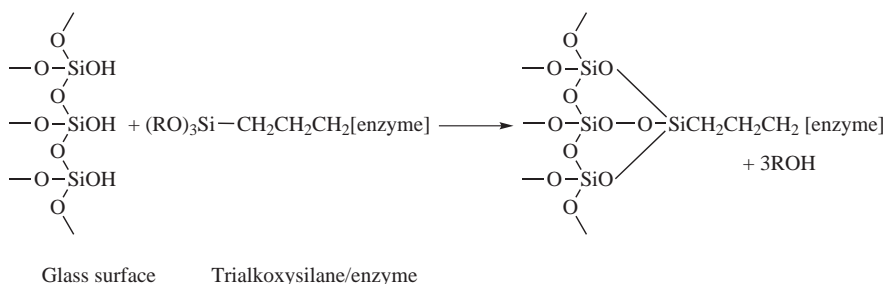
In all likelihood, the enzyme is not truly “fixed” and retains some ability to accommodate itself to the shape and conformation of the molecules whose chemical reactions it is catalyzing. Similarly, the substrate to which the enzyme attaches must be able to accommodate to the shape presented by the enzyme. The “immobilization” means that enzymes can be reused many times in continuous reactors. Enzymes are manufactured in bulk by conventional fermentation techniques. They are immobilized in various ways. For intracellular enzymes, either the cells are stabilized by entrapment in an aqueous gel or attached to the surface of spherical particles, or they are homogenized and crosslinked onto glass with glutaraldehyde, $\text{OHCCH}_2\text{CH}_2\text{CH}_2\text{CHO}$, to form an insoluble yet penetrable matrix.

Extracellular microbial enzymes are immobilized in the form of proteins purified to varying degrees. This usually involves the coupling of the free amino groups on lysine $[\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}(\text{NH}_2)\text{COOH}]$ residues within the enzyme onto a substrate, again with glutaraldehyde, to give an insoluble, active, stabilized enzyme.

There are more sophisticated, less widely used methods. Thus one may start with polystyrene lightly crosslinked with divinylbenzene to give a gel. Treatment with formaldehyde, hydrochloric acid, and zinc chloride gives a chloromethylated polystyrene, in which some of the benzene rings contain $-\text{CH}_2\text{Cl}$ groups and these will react with amino groups on the enzyme to bind it to the polymer.

Another method uses trialkoxysilanes as coupling agents. A range of agents are available and they couple with enzymes to give compounds of the type

[enzyme]—CH₂CH₂CH₂—Si(OR)₃. The three carbon bridge is sufficient to ensure that the active site of the enzyme is not obstructed on immobilization. The trialkoxysilicon group will bind to a glass surface to immobilize the enzyme:



18.8.1 Catalytic Antibodies

Catalytic antibodies are an exciting area of catalyst development in the pharmaceutical industry.¹⁸ Antibodies are chemicals produced by the body as part of its defense against antigens, that is, infecting organisms (pathogens) or their toxic products. Cells may be stimulated by infection to produce these antibodies. A person infected with measles, for example, develops the measles antibody and does not get the disease a second time. Immunization with attenuated measles virus produces the same effect. An alternative method, known as passive immunization (e.g., for diphtheria) is to inject the antibodies (immunoglobulins) from one person into another. Once an antibody has been identified, it is also possible by genetic engineering techniques to develop cells that will yield larger quantities of it. The technique is an elegant way to produce enzymes to order. The interaction between an antigen and its antibody is chemical and specific. A known antigen can be used to identify an unknown antibody and vice versa. Antibodies can be isolated.

An early example of the sort of reaction that can be carried out with the aid of catalytic antibodies was the selective catalysis of an unfavorable reaction pathway. In the normal way, the hydroxyepoxide (**XV**) (Fig. 18.8) cyclizes spontaneously to the substituted tetrahydrofuran (**XVI**). The aim of the researchers was to direct the reaction toward the disfavored tetrahydropyran (**XVII**). They first synthesized a hapten. A hapten is a small molecule that reacts with proteins, polypeptides, or other carrier substances to give an antigen. In this case, an *N*-oxide hapten (**XVIII**) was synthesized, which resembled the transition state of the disfavored reaction pathway. It was injected into an animal and induced a range of antibodies against an antigen that had the structural features of the transition state. The researchers extracted and purified 26 antibodies and evaluated their catalytic properties. Two of them were regioselective for the formation of the desired product and one was highly stereoselective, so that the desired tetrahydropyran resulted.

Catalytic antibodies have recently been reported that catalyze peptide bond formation without the need for multiple protecting groups and without residual

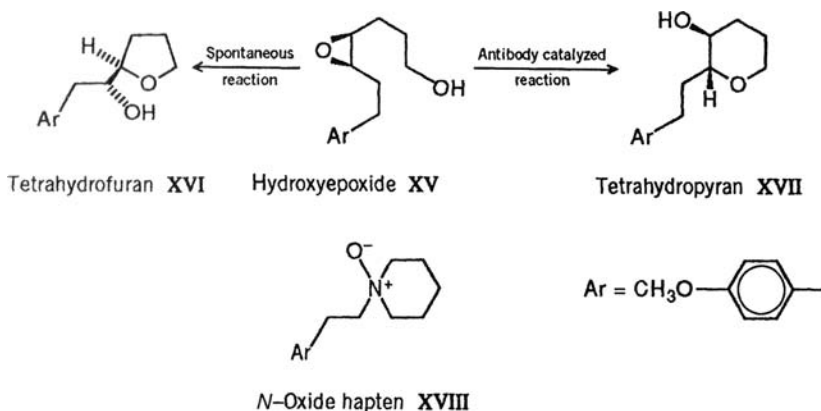


FIGURE 18.8 Antibody-catalyzed reactions.

hydrolytic side reactions. Peptide synthesis is potentially an important branch of biotechnology.

18.9 SHAPE-SELECTIVE CATALYSTS

Porous solids are designated microporous if their pores are less than 2 nm in diameter, mesoporous if they are between 2 and 50 nm, and macroporous if they are larger. Microporous aluminosilicate minerals are known as zeolites. Many naturally occurring clays and minerals are microporous and may be used as adsorbents (e.g., Fuller's earth as cat litter), drying agents, and supports for catalysts. Zeolites are widely used in industry for water purification, as catalysts, and in nuclear reprocessing. Their biggest use is as builders in laundry detergents, to remove calcium ions from the water. Synthetic zeolites with uniform and structured porosities are available. These act as specific catalysts, which not only bring about selective chemical reactions but can even generate greater-than-equilibrium concentrations of products.

Zeolites have a three-dimensional polymeric framework. Their basic building block is a tetrahedral unit with a silicon or aluminum atom (the so-called T-atom) at the center and oxygen atoms at the corners (Fig. 18.9a). Each oxygen atom is bonded to a further T-atom; that is, it is shared with another tetrahedral unit. The T-atoms can unite via T–O–T linkages to give squares (Fig. 18.9b) or hexagons (Fig. 18.9c) of T-atoms. Combination of these square and hexagonal units gives the sodalite cage (Fig. 18.9d), a basic substructural unit. The sodalite cage has oxygen atoms with free bonds able to link to other sodalite cages.

If the sodalite cages unite via their hexagonal faces, an X- or Y-type zeolite is obtained (Fig. 18.9e). These have voids in the center, called supercages, with a diameter of 1.3 nm, and pores or apertures leading to them with a diameter of 0.74 nm.

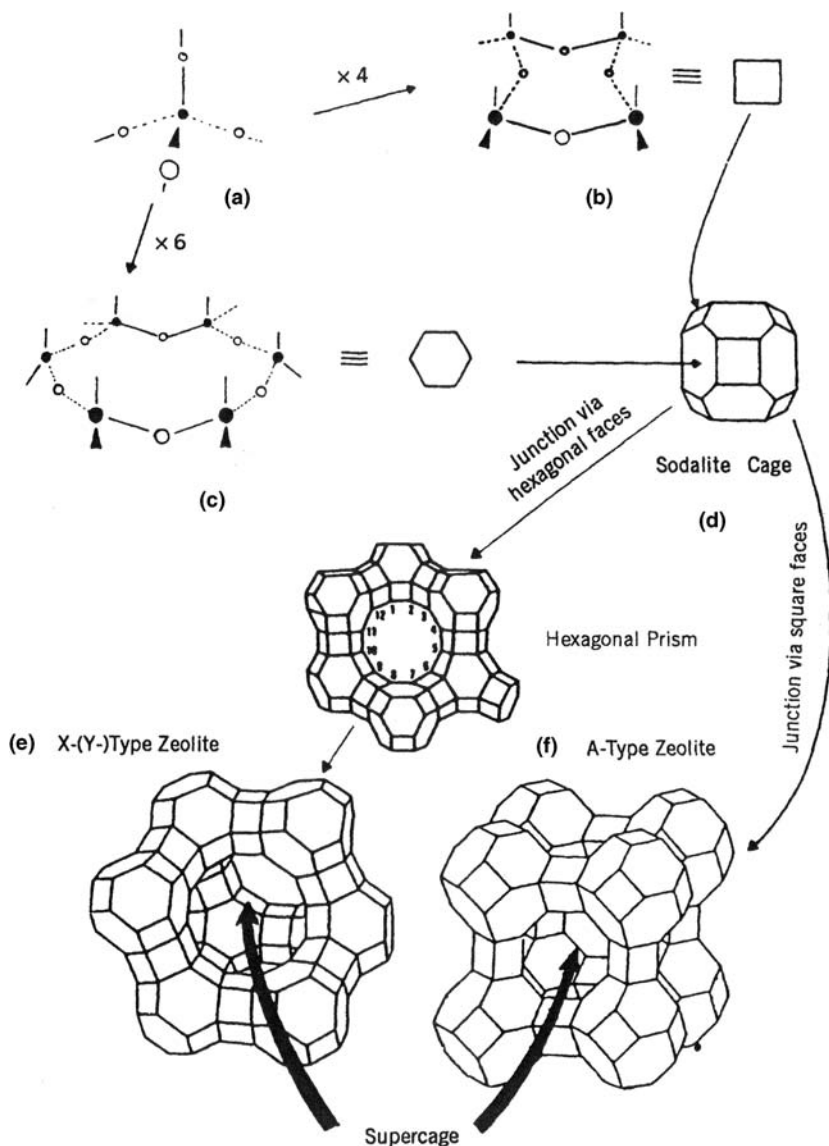


FIGURE 18.9 Basic structural units and the modes of their combination in the common zeolites. T atoms (Si or Al) are denoted as \bullet in the simple structures and lie at the intersections of lines in the complex structures. Oxygen atoms are shown in the simple structures when they are represented as \circ : in the complex structures an oxygen atom lies at the midpoint of each line. Reproduced from *Biomass, Catalysts and Liquid Fuels*, I. M. Campbell (1983), Holt, Rinehart and Winston Ltd. Eastbourne, p. 116, with permission.

If the sodalite cages unite via their square faces, an A-type zeolite (Fig. 18.9f) is obtained with supercage diameter 1.1 nm and pore aperture 0.42 nm.

Zeolites are typically made from a mixture of sodium aluminate and sodium silicate (or silicic acid) in a temperature range between 300 and 450 K under moderately hydrothermal conditions. Hydrothermal synthesis grows single crystals based on the solubility of minerals in hot water under high pressure. It is performed in an autoclave, and a temperature gradient is maintained between the opposite ends of the growth chamber, so that the hotter end dissolves added materials and the cooler end causes seeds to take additional growth.

As initially obtained, the zeolite crystals contain water, which solvates the ionic sites within the structure. This is driven off by heating to 600–700 K. To obtain catalytic activity, it is necessary to replace sodium ions Na^+ by H^+ . This is achieved by immersing the solid in concentrated ammonium nitrate solution. Ion exchange gives an ammonium zeolite, and heating to 700 K thermally decomposes the ammonium ion to generate ammonia and leave an acidic form of the zeolite with “holes” where the sodium ions were. Such acid species are designated by an H preceding their names. For example, the acid form of ZSM-5 is called HZSM-5.

In a significant development, Mobil included tetrapropylammonium ions instead of sodium ions in the parent solutions. Between 40% and 90% (typically 70%) of sodium ions were replaced in this way. $(n\text{-C}_3\text{H}_7)_4\text{N}^+$ ions are much bigger than Na^+ ions and the resulting zeolite had a structure intermediate between those of the A- and X- or Y-type zeolites. It was called ZSM-5. (The SM in the name stands for Socony Mobil, the company where the catalyst was invented and the Z, of course, stands for zeolite.) Incorporation of tetramethylammonium ions as a template led to offretite, and tetrabutylammonium ions to ZSM-11. Mobil discovered ZSM-5 in 1968 but failed to recognize its activity for five years. Mobil then found it would convert methanol by way of dimethyl ether to a gasoline containing aliphatic compounds and mixed aromatics up to durene (1,2,4,5-tetramethylbenzene). It also provided aromatics from paraffins, olefins, and oxygenated material and can thus be used to increase the octane number of gasoline. Fischer–Tropsch hydrocarbons (Section 14.2) have an octane number of about 60, and passage over ZSM-5 can raise this to 90. The major use for ZSM-5 is for xylene’s isomerization, discussed below. It catalyzes the disproportionation of toluene to benzene and *p*-xylene (Section 10.1) and is important in one process for the condensation of benzene and ethylene to ethylbenzene (Section 5.8) as well as the condensation of benzene and propylene to cumene (Section 6.6).

Pores and voids make up about half the volume of zeolites but these “holes” are not accessible to all molecules. Small molecules can diffuse in and out with ease, but larger ones cannot. A-type zeolite admits *n*-alkanes but not branched chain alkanes. Benzene is also rejected. There is thus a *molecular sieve* action. Sometimes, this provides a method of separation, such as straight chain from branched chain hydrocarbons. In other cases, molecules are excluded from catalytic sites on account of their size. Molecules that do gain access to the voids, however, are subject to strong localized electrostatic fields. In most current industrial applications, this leads to acid catalysis.

The shape selectivity of a zeolite catalyst may apply to the reactants, the transition state, or the products. An example of reactant selectivity used to raise the octane number of gasoline is the cracking of straight chain alkanes over A-type zeolites. Branched chain materials are excluded from the acid sites. Over an amorphous silica-alumina, the branched chain alkanes would be preferentially cracked or isomerized.

An example of product selectivity is the transalkylation of toluene over HZSM-5 modified with magnesium and phosphorus. The products are benzene and *p*-xylene (Section 10.1). Benzene diffuses very rapidly out of the pores. *p*-Xylene diffuses moderately fast, while the other two isomers diffuse at 0.1% of the rate of the *p*-isomer. Thus they have a high chance of isomerizing again before they escape. At operating temperatures, the thermodynamic distribution of xylenes is about 25% *ortho* and *para* and 50% *meta*; zeolites are claimed to give 88–95% *para*.

The most important example of transition-state selectivity is the absence of coking in such processes as the formation of gasoline from methanol over HZSM-5 in the Mobil process. Coking proceeds via polynuclear aromatic hydrocarbon intermediates, but the zeolite discriminates against molecules with more than 10 carbon atoms. Hence coking is avoided and the spread of molecular weights is narrow compared to products from the Fischer–Tropsch or similar processes.

The Mobil process still appears to be the cheapest route to gasoline-from-methanol but for many years it was commercialized only in New Zealand. There has been much renewed activity in the 2000s, because of the convenience of converting “stranded” natural gas into methanol. Toluene disproportionation, however, has been widely commercialized.

The number of commercialized processes involving synthetic zeolites is growing and Table 18.3 shows areas of interest. There is extensive research in progress on microporous aluminophosphates, showing that silica is no longer necessary in the formation of a molecular sieve. A British group has converted hexane to adipic acid at low temperature by means of an aluminophosphate molecular sieve with cobalt(III) ions located on the inner walls of cages inside the sieve. Yields at the time were only 30%. The same group converted cyclohexane to adipic acid by air oxidation using an aluminophosphate sieve containing iron(III) ions. Yields were poor (33% for the cyclohexane), but these processes are early examples of extra-large pore molecular sieves where catalytically active metal atoms are deposited in the pores to give “uniform” heterogeneous catalysts. Active sites are distributed in a spatially uniform way throughout the bulk of the solid.¹⁹

Another zeolite-catalyzed oxidation process is Solutia’s nitrous oxide-based oxidation of benzene to phenol (Section 9.1). This reaction is reportedly catalyzed by ZSM-5 or ZSM-11 incorporating iron. Among other things, these oxidations confirm the possibility of zeolite and sieve-based industrial processes other than acid catalysis. Dendrimers offer related opportunities (Section 17.4.4). Shape-selective catalysis is intriguing and holds great potential.

Current research is focused on hierarchical zeolites. These are characterized by different porosity levels within the zeolite. The aim is to retain the catalytic activity of the zeolite while, at the same time, enabling simple access of reactants and egress of

TABLE 18.3 Catalytic Effects of ZSM-5 and Other Zeolites

Zeolite	Reaction	Reported Results
ZSM-5	Butene aromatization	Increased stability
ZSM-5	Liquid phase HDPE degradation	Higher catalytic activity
ZSM-5	N ₂ O-mediated benzene to phenol	Higher yield to liquid products Increased lifetime Higher phenol yield and selectivity
ZSM-5	Methylation of 2-methylnaphthalene	Increased lifetime Higher activity
ZSM-5	Synthesis of pyridine and pycolines	Increased stability
ZSM-5	Cracking of cumene and heavy oil	Higher cracking activity Higher yield to light olefins
ZSM-5	Methanol to gasoline	Increased gasoline fraction (C ₅ +) Higher propylene:ethylene ratio Increased lifetime
ZSM-5	Methanol to propylene	Higher propylene selectivity Higher propylene:ethylene ratio
ZSM-5	Benzene alkylation: with ethylene	Higher ethylbenzene yield
ZSM-5	Aromatization and isomerization of 1-hexene	Improved lifetime
ZSM-5	Cracking of <i>n</i> -octane	Higher activity Higher propylene selectivity Reduced oligomerization
ZSM-5	Oligomerization of styrene	Higher activity Higher selectivity
ZSM-5	Isomerization of α -pinene	Higher activity and yield to products
LaZSM-5	Liquid-phase LDPE degradation	Higher activity Higher liquid quality
MoZSM-5	Methane dehydroaromatization	Higher activity and selectivity to aromatics Higher tolerance to coking
FeZSM-5	N ₂ O decomposition	Higher activity
ZnZSM-5	I-Hexene isomerization	Higher stability

Source: *Novel Concepts in Catalysis and Chemical Reactors*, eds. A. Cybulski, J.A. Moulijn, and A. Stankiewicz, Wiley-VCH, Weinheim, 2010.

products from the micropores. A purely microporous zeolite is said to be nonhierarchical. Increase in pore size is generally brought about by displacement of a metal atom. Silica, aluminum, titanium, and other ions within the zeolite may be removed by complexing, leaving relatively large holes within the structure.²⁰ Cavities of up to 1.25 nm can be produced surrounded by rings of 12 or more T-atoms.

Metal–organic frameworks (MOF) are another area of interest for shape-selective catalysis and adsorptive separations.²¹ They consist of metal ions or clusters linked by

organic molecules, usually rigid, to give porous networks. Copper and zinc are the most widely investigated metal ions. Linkers can be bidentate, for example, terephthalic acid or oxalic acid; tridentate such as citric acid; or azoles such as 1H-1,2,3-triazole. They can be crystallized in complex porous structures that evidently have catalytic properties. Meanwhile, the interest in them is chiefly on the grounds that they will absorb huge amounts of gases, and they could be an answer to how to store hydrogen in a hydrogen-fueled vehicle. They might also be of value in fractionating gases.²²

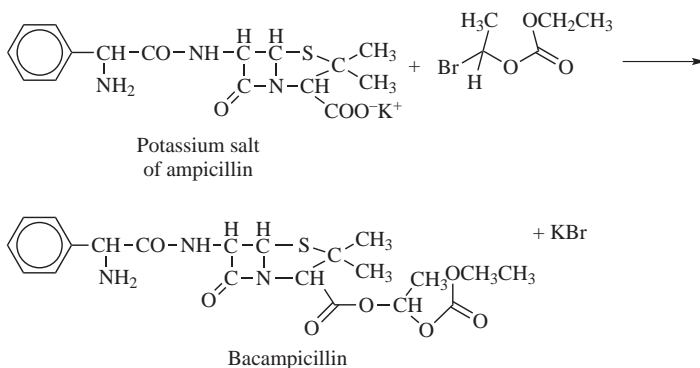
Related to work on zeolites and metal-organic frameworks is research on clay minerals and particularly smectite clays. These are aluminosilicates like zeolites and consist of layers, the separation of which can be varied and between which catalysts can lodge. They are known as intercalated catalysts. The collapse of the layered structure at temperatures above 200°C may be avoided by incorporation of “spacers” such as aluminum or zirconium hydroxides to give so-called pillared clays. Currently, the only commercial process based on smectite clays is the dimerization of oleic acid (Section 15.5).

There seems to be little commercial interest in these materials at present, but they still have some remarkable properties. For example, magnesium, nickel, and magnesium-nickel smectite catalysts containing different amounts of sodium, potassium, and lithium will selectively convert propylene and carbon dioxide to propylene carbonate.²³ Also, smectite catalysts, when illuminated with UV light, will disinfect bacteria-contaminated water.²⁴

18.10 PHASE-TRANSFER AND FLUOROUS BIPHASE CATALYSIS

Phase-transfer catalysis is used for the preparation of polycarbonates (Section 9.1.2.2), estradiol carbamate, and various fine chemicals. It is not likely to be involved in the manufacture of large tonnage heavy organic chemicals but is an unusual and elegant catalytic technique that is energy-sparing and gives high yields at low residence times under mild conditions. It is therefore typical of the methods that will be attractive in the future.²⁵

It finds application where reactants are immiscible. An example is the production of penicillin esters in which the free carboxyl group of the aminopenicillanic acid is esterified with a labile group that will hydrolyze in the gut.²⁶ The desired reaction is



but the ampicillin salt is water-soluble, whereas the acid chloride dissolves in organic solvents and would be hydrolyzed by water. Mild conditions are essential to avoid decomposition of the acid chloride and the lactam ring of the ampicillin. The acid chloride is therefore dissolved in an organic solvent such as dichloromethane or chloroform and brought into contact with an aqueous solution of the ampicillin salt at 25°C. A phase-transfer catalyst such as tetrabutylammonium chloride is added to the aqueous phase.

A simple interpretation of what occurs is that the tetrabutylammonium cation is lipophilic and migrates into the organic layer as an ion pair carrying with it the ampicillin anion, which is less hydrophilic than the other anions present. Esterification of the ampicillin anion then takes place in the organic layer, and the tetrabutylammonium ion pairs with the chloride ion that is generated. The latter is so hydrophilic that it carries the tetrabutylammonium cation back into the aqueous phase and the procedure is repeated until esterification is complete. Kinetic measurements indicate that the mechanism is more complicated and may involve inverse micelle formation and interfacial reactions.

An opportunity for phase-transfer catalysis to be used in a large-tonnage process was frustrated by environmental considerations. Ethylene dibromide is at present made by bromination of ethylene. The elemental bromine is obtained from bromide-containing brines from which it is displaced by chlorine and steam in an expensive energy-intensive process. Dead Sea Bromine, in Israel, developed a process by which ethylene dichloride was mixed with Dead Sea brines in the presence of a phase-transfer catalyst. Bromine is more lipophilic than chlorine; hence the bromide ions were carried to the organic layer to yield the dibromide. The main use for ethylene dibromide, however, was as a lead scavenger in leaded gasoline. Its market therefore declined and it was never worthwhile to commercialize the process.

Fluorous biphasic catalysis is a further technique involving phase separation.²⁷ At low temperatures, many systems consisting of an organic and a fluorinated solvent such as toluene and perfluoro(methylcyclohexane) are immiscible but, on heating, the solvents coalesce to a single phase, allowing homogenous reactions to take place. An example given in the literature and shown in Figure 18.10 shows the selective hydrogenation of the carbon–carbon double bond in cyclohexenone. Cyclohexenone in toluene is brought into contact with gaseous hydrogen and a solution of a rhodium catalyst in perfluoromethylcyclohexane. The phases do not mix and there is no reaction. On heating to 45°C, the organic layers become miscible and hydrogenation takes place. The system is cooled and vented. The catalyst-containing phase reappears and can be recycled.

18.11 NANOCATALYSIS

Nanoscience and nanotechnology have been one of the growth areas in chemistry over the past decade. These topics stemmed from a realization that there was not a sudden jump from the properties of a single atom or molecule to the properties of the bulk material. An atom or molecule has discrete well-defined

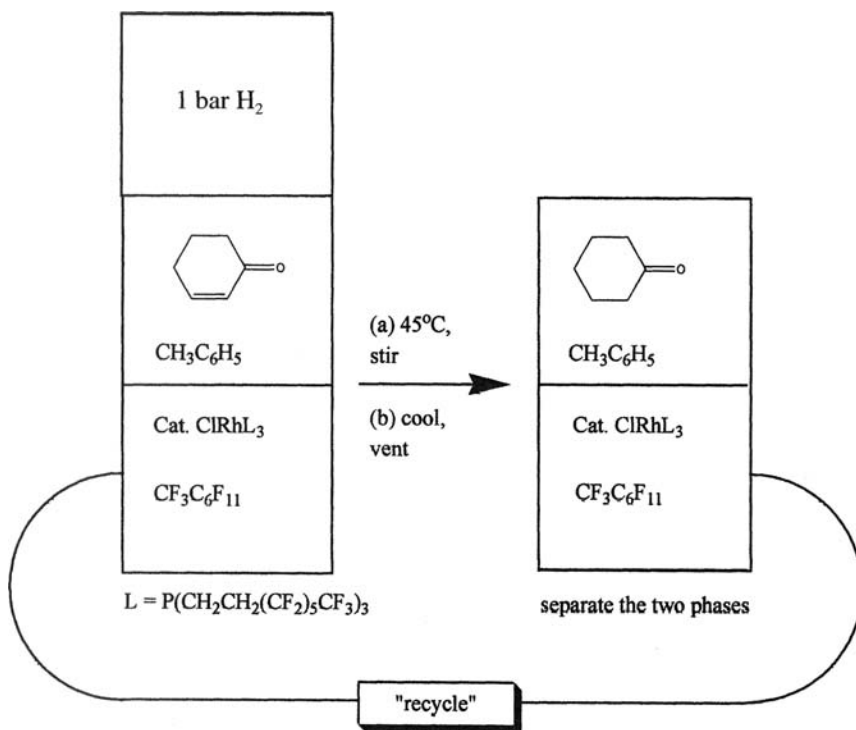


FIGURE 18.10 Fluorous rhodium-catalyzed alkene hydrogenation.

energy levels. Bulk materials have more or less continuous energy levels, with well-defined valence and conductor bands. In-between, for clusters between 1 and 100 nm, band structures are building up; statistical and quantum mechanical effects come into play. In addition, there is a huge increase in surface-to-volume ratios, and the atoms near the surface or at the edges of nanoparticles have lower coordination numbers than in the bulk material. All these factors can lead to greatly increased reactivity. To put these sizes into perspective, a 1 nm particle will typically contain about 50 atoms and a 10 nm particle about 50,000. Thus large molecules such as enzymes can behave individually as nanoparticles, and many of the classic metal catalysts deposited on high surface area supports are actually deposited as nanoparticles.

Gold nanoparticles, in particular, have attracted attention. Bulk gold is distinguished by its lack of reactivity but, in the form of nanoparticles with diameters less than about 5 nm, it becomes a powerful catalyst for the oxidation of carbon monoxide, at temperatures as low as 200 K, and the hydrochlorination of acetylene. The reactivity depends primarily on the particle size [a $1/(\text{diameter}^3)$ relationship] and to a lesser extent on the support, for example, silica, titania, or alumina.

For oxidation of carbon monoxide at room temperature, gold deposited on reducible metal oxides such as TiO_2 , Fe_2O_3 , Co_3O_4 , NiO , and CeO_2 is much more

active than platinum group catalysts. Carbon monoxide is adsorbed at the edges, corners, and steps of the gold nanoparticles. Oxidation takes place at the junction between the gold and the metal oxide support.²⁸

Oxidation of carbon monoxide at ambient temperatures is a desirable objective. In the United States in 2009, 4000 people had to be taken to hospital, and 10% of them died from carbon monoxide from poorly ventilated boilers. Gold nanoparticles could prevent this and, already, respirators are on the market to protect firefighters and miners from carbon monoxide poisoning.²⁹

Industrial applications include the production of vinyl acetate (Section 5.6) and the hydrochlorination of acetylene. BP (now INEOS) commissioned a gold-catalyzed 250,000 metric tons/year vinyl acetate plant in Hull in 2001. The acetylene application may become part of the revival of acetylene chemistry. The traditional hydrochlorination catalyst was mercuric chloride, a highly toxic material, which inevitably finds its way into the environment. Replacement of mercury by gold in this and various other applications may have economic benefits, and it is also likely that the EPA will impose stringent regulations on mercury emissions.

A further application is the use of gold–palladium nanoparticles for breaking down trichloroethane and other chlorinated hydrocarbons in wastewater.

Nanocatalysts may be produced by either top–down or bottom–up techniques. The former involves physical methods such as crushing and pulverization. Electron beam lithography permits the machining of metal blocks on a scale of tens of nanometers. Bottom–up methods include the deposition of nanoparticles from a supersaturated vapor and the decomposition or reduction of metal salts or organometallics. In the latter case, the nanoparticles are produced as a hydrosol. By using a metal salt in solution such as hexachloroplatinic acid or rhodium acetylacetonate as a precursor monomer, it is possible to produce monodisperse metal nanoparticles, each coated with surfactant or a polymer layer that prevents their aggregation in solution. For example, a mixture of rhodium(III) acetylacetonate and platinum acetylacetonate in $C_4H_8(OH)_2$ under argon at 170–230°C in the presence of poly(vinylpyrrolidone) with a chain length of about 500 gives a fairly narrowly defined yield of $Rh_{40}Pt_{60}$ nanoparticles.³⁰

A novel method of producing nanocatalysts is by means of dendrimers (Section 17.4.4) such as poly(amidoamine)(PAMAM). As a first step, metal precursors such as $Cu(OH_2)_6^{2+}$, $PdCl_4^{2-}$, or $PtCl_4^{2-}$ are intercalated through the porous exterior of PAMAM, and they complex with the interior amine and/or amide groups. Electrons are added via borohydride ions BH_4^- , which reduce the metal ions to metal nanoparticles held within the dendrimers. These are called dendrimer encapsulated nanoparticles (DENS) and are of a uniform size because the dendrimer acts as a template.

Subnanometer sized metal particles containing a well-defined number of atoms can be produced by this method. For example, a novel dendrimer has been developed based on phenylazomethine units that form one-to-one complexes with platinum salts, arranged around a tetraphenylmethane core. By treating the dendrimer with measured equivalents of platinum chloride, dendrimers with defined numbers of platinum atoms can be produced, and on reduction the platinum atoms coalesce into

size-selected clusters within the dendrimer. They have an unexpectedly high activity in oxidation–reduction reactions.³¹

The DENs may sometimes be used as catalysts without further treatment. The nanocatalysts may also be extracted from the dendrimer, for example, with toluene-containing thiols, where the thiols assemble on the surface of the nanoparticles and transport it to the toluene phase. The “empty” dendrimer may then be recycled to produce more nanoparticles. Heterogeneous catalysts have also been prepared via dendrimers. In one example, PAMAM dendrimers were first used to prepare platinum nanoparticles in solution. The DENs were then deposited on a high surface area silica support and the dendrimer removed by heating to leave an oxidation/hydrogenation catalyst.³²

A sequential reduction may be used to give bimetallic catalysts. The preparation starts with the complexation and reduction of a “seed” metal M_a followed by the complexation and reduction of a second metal M_b to give an M_aM_b system. Such bimetallic catalysts are especially active.^{33–37}

18.12 CATALYSTS OF THE FUTURE

The main areas of catalyst growth in the immediate future are seen as the following:

- Enzymes for biofuels and other biotechnology
- Hydrocracking and hydrodesulfurization catalysts for the upgrading of heavier petroleum fractions⁹
- Polymerization catalysts – mainly organometallics and single site catalysts – because of the growth of the polymer industry in Asia-Pacific
- Catalysts for increased propylene production

The more diffuse general objectives seem to be as follows.

18.12.1 Catalyst Design

An objective is to advance catalyst theory to the point where catalysts can be designed. Remarkable progress has been made in the past few years in understanding catalyst action. The use of computer modeling, routine for many years in the development of new pharmaceuticals, is now being used in the design of catalysts.³⁸ Computer techniques can aid catalyst design not only at the molecular and electronic level but also in the modeling of transport phenomena. The work on metal–organic frameworks and hierarchical zeolites is a step in this direction. There is scope for a breakthrough.

18.12.2 Higher Selectivities

A further aim is to achieve higher selectivities in known reactions. This might involve improvement of existing catalysts or development of new ones. Most of the catalysts

discussed earlier were developed primarily to give higher selectivities, and we may expect to see advances in, for example, catalysis by zeolites.

Ammonoxidation of propylene to acrylonitrile (Section 6.5) shows what is possible. The earliest catalysts (in the laboratory) gave 6% yields. Bismuth phosphomolybdate raised this to 65% and a plant was built in 1959. An antimony–uranium oxide catalyst gave laboratory yields of 80% in 1966 (72.5% in the plant). In 1972, promoted bismuth–molybdenum oxides on silica raised plant yields to 77%. A fourth generation catalyst composed of an oxide complex of iron, selenium, and tellurium appears to give about 83% and a series of patents in the early 1980s claimed 87% for a related complex. In the 1990s, the newer catalysts have reduced by-product acetonitrile production to the point that there is a shortage for the small volume uses that do exist. Asahi and BP have developed more active catalysts with longer lives and these have produced further challenges. With high activity catalysts, less needs to be used. The surface area of the catalyst bed is thus reduced and heat removal becomes more difficult. Mitsubishi Chemical has designed a special fluidized bed reaction that enhances the contact between the gaseous reactants and the catalyst.³⁹

Catalysts for syngas conversion are a priority. The main interest is in syngas to hydrogen and syngas to methanol, but there is still scope for improvement in the classic iron catalysts for the Haber process for ammonia.⁴⁰ Yields in the mid-1990s were between 15% and 17% per pass. Kellogg and BP then reported a new catalyst with ten to twenty times greater activity (Section 12.5.1). It was more tolerant to variations in the $N_2:H_2$ ratio. The saving in energy was estimated at 21 kJ/mol and the saving in cost at \$2–6 per metric ton of ammonia. Other workers have reported promoted catalysts containing Fe_3Mo_3N , Co_3Mo_3N , and Ni_2Mo_3N , but it is not clear which of these has been commercialized. The use of membranes to permit recycling of unreacted hydrogen and thereby preventing buildup of argon was a significant advance but not in catalysis. The Haber process is said to account for 1% of world energy consumption. Hence there is a great incentive for improved catalysts, but there are formidable difficulties in finding them.

18.12.3 Catalysts with Greater Activity

An objective is to synthesize catalysts with greater activity (e.g., Ziegler catalysts as in Section 18.1.2). Greater activity improves economics. An important goal is the synthesis of homogeneous catalysts with high enough activity for conversion to heterogeneous catalysts that still retain activity. Enzymes may be immobilized without substantial loss of activity but, in general, only a highly active homogeneous catalyst can be immobilized successfully.

There has been considerable interest in the use of clusters of metal atoms bound to carbon monoxide as highly active catalysts. Many catalytically active metals such as palladium, rhodium, platinum, osmium, rhenium, and ruthenium form clusters. $Rh_6(CO)_{16}$ is active in the methanol/CO route to acetic acid, but appears to cleave during the reaction. In spite of much research, cluster catalysts have not yet been commercialized.

Nanocatalysts (Section 18.11) are an attractive prospect as are intermetallic compounds. Many of these are known, one component being a rare earth. Lanthanum pentanickel, LaNi_5 , for example, absorbs large quantities of hydrogen reversibly and may be used in low temperature hydrogenations. Currently, $\text{Rh}_6(\text{CO})_{16}$ is used in acetic acid production. Sometimes the two metals may be bonded either directly or via a ligand. One metal activates a hydrogen atom and the other the molecule.

There is also interest in the catalytic properties of heteropolyacids. An example that has been commercialized is the production of *t*-butanol from the isobutene in mixed butenes over the heteropolyacid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$.

18.12.4 Pollution Problems

Catalysts are needed to solve pollution problems. The breakthrough in this area was the development of the platinum–palladium–rhodium catalysts that oxidize unburned hydrocarbons and carbon monoxide in the catalytic converter of automobiles. All the same, a cheaper catalyst is a desirable aim, as is a catalyst that would promote decomposition of nitrogen oxides to molecular nitrogen and oxygen in the presence of water and carbon dioxide. Nanostellar, California, has recently developed an auto catalyst in which gold partially replaces the more expensive platinum.²⁹ Given the recent surge in gold prices, it is hard to see gold as a cheap replacement for anything.

Other needs are for catalysts to desulfurize flue gases and to remove organochlorine compounds from water. The latter might involve hydrogen or hydrogen donors such as hydroaromatics, and a catalyst, based perhaps on iron, cobalt, or ruthenium. There are a host of other environmental problems that could be helped by novel catalysts.

18.12.5 Catalysts for New Reactions

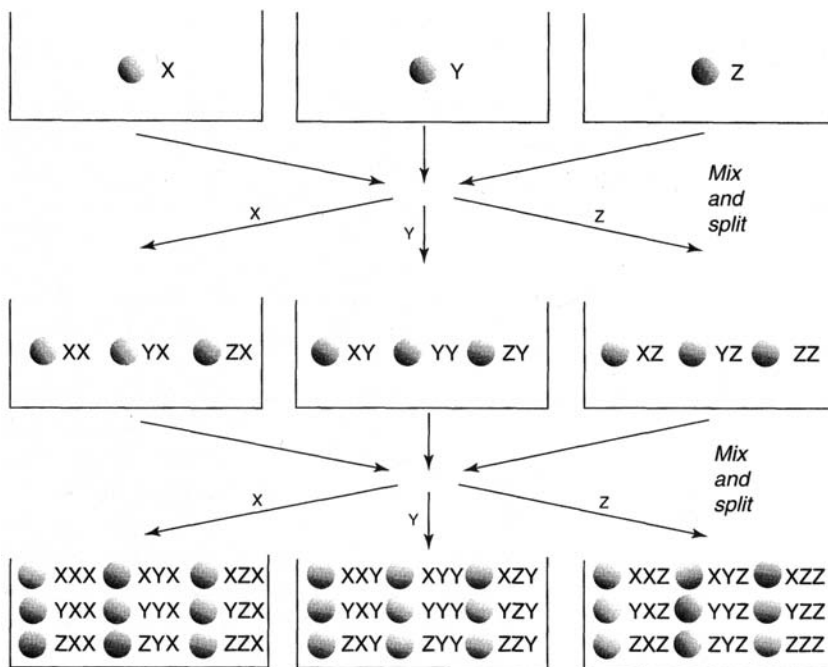
Catalysts are needed for new reactions. A major research aim today is the functionalization of methane,⁴¹ ethane, propane, and butane to replace more expensive olefins as petrochemical precursors. Selective catalysts for low temperature liquid phase oxidation of methane to methanol and for oxidative coupling of methanol to ethylene would be especially valuable (Section 13.1). Among the few successes so far in the functionalization of alkanes is the conversion of *n*-butane to maleic anhydride (Section 7.4.2). Processes for conversion of propane to acrylonitrile and ethane to vinyl chloride were slated for commercialization in the mid- to-late 2000s but progress has been slow (Section 13.2.1). A laboratory process, typical of many, has also been reported for direct conversion of methane to acetic acid in aqueous solution at 100°C. The oxidants are carbon monoxide and oxygen and the catalyst rhodium trichloride plus a source of iodide ions or 5% palladium on carbon.

18.12.6 Catalysts that Mimic Natural Catalysts

Catalysts are needed that mimic natural catalysts. Nature manages to produce complex organic molecules in a single stereochemical form under mild conditions. The synthesis of stereoregular and optically active compounds is already possible in some cases (Sections 18.7.1 and 18.7.2). Some natural enzymes may be isolated, immobilized, and used as catalysts to give “natural” products. Most remarkable of all is recombinant DNA engineering or gene splicing, which makes possible the synthesis of proteins and peptides.

18.12.7 Catalyst Discovery Via High Throughput Experimentation

Combinatorial chemistry was first developed to speed the synthesis and discovery of pharmaceutically active compounds, but these methods have since been adapted for



Note: Mix and split synthesis: using three reagents bound to resin beads, a library of 27 products can be generated in just three steps

FIGURE 18.11 Combinatorial chemistry. (Source: D. J. Tapolczay, R. J. Kabyleck, L. J. Payne, and B. Hall, Extracting order from chaos, *Chem. Ind.*, 1998, pp. 772–775.)

wider applications, in particular, catalyst development. The term combinatorial chemistry covers a variety of synthetic methods, but the basic concept is simple. Techniques are used that quickly generate a vast collection of compounds that might be therapeutically or catalytically active or whatever is sought. Figure 18.11 shows the generation of a library of 27 compounds in just three steps, starting with the reagents X, Y, and Z bound to polymer beads. Treatment of these entities with further reagents X, Y, and Z generates nine compounds and, if these are mixed and split again, 27 compounds have been generated after a relatively small number of operations. The compounds can then be displaced from the beads and screened. The deconvolution technique to identify the active compound is similar but in reverse. Combinatorial chemistry provides libraries of novel compounds at a rate perhaps a thousand times greater than if they are synthesized by conventional laboratory chemistry.

In order to take advantage of combinatorial chemistry, however, techniques for rapid screening, analyzing, data manipulation, and interpretation must also be developed. The broad term used to cover this activity is high throughput experimentation or HTE.

The first independent company established to exploit combinatorial chemistry and HTE for developing commercially useful materials was Symyx Technologies, California, founded in 1994. Symyx screens over one million new materials per year with applications ranging from X-ray storage phosphors to polymers for DNA and including research into new catalysts for the manufacture of chemicals and plastics. In April 2003, Dow Chemical and Symyx jointly claimed to have discovered by HTE a new class of single-site polyolefin catalysts composed of amide-ether-based hafnium complexes. Other companies have since been established for developing new catalytic materials including HTE AG in Germany, Avantium in Holland, and Torial in the United States.

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CHAPTER 19

Green Chemistry

Green chemistry – the idea that chemical processes should avoid damage to the environment – has been a stated aim of the chemical industry for the past two decades. It has moral overtones but is also predicated on a belief that neglecting environmental considerations will not only make people’s lives worse but will, in the end, damage the chemical industry itself. The use of sustainable technologies benefits industrialists just as much as customers in the long term. One can do well by doing good.

Green chemistry is a subset of industrial organic chemistry, the theme of this book. Just as industrial chemistry focuses on the chemical reactions that are characterized by simple, cheap reagents operating on intermediates obtained in a small number of steps from cheap and readily available feedstocks, so green chemistry focuses on the environmental implications of industrial chemical processes. The twelve commandments of green chemistry are displayed in Table 19.1. These represent an ideal – few chemical processes could comply with every one of the commandments – but they provide a standpoint from which technologies can be viewed. We emphasize that the emergence of green chemistry as a discipline in the early 1990s does not imply that chemists before that date were indifferent to environmental considerations. After all, the development of the Leblanc process saved the forests of Europe. The use of by-product hydrogen chloride from the Leblanc process to make bleaching powder in the nineteenth century reduced acid pollution of the countryside around Widnes, England. The subsequent replacement of the Leblanc process by the Solvay process was a further step toward a cleaner alkali industry. Baekeland’s invention of phenolic resins obviated the need to kill elephants for ivory for billiard balls. The improvement of processes in general increases yields, which improves profitability, and it also decreases by-products and emissions. Replacement of traditional catalysts by others that are less toxic, more specific, and more easily separated from product are an important source of “greening.” The improvement in propylene polymerization (Section 6.2.1) is an excellent example, as are the production of bisphenol A with a solid catalyst rather than hydrochloric acid (Section 9.1.2) and the production of cumene with a solid catalyst rather than aluminum chloride or phosphoric acid (Section 6.6).

TABLE 19.1 The Twelve Commandments of Green Chemistry

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- 1. Prevention.** It is better to prevent waste than to treat or clean up waste after it has been created.
 - 2. Atom economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
 - 3. Less hazardous chemical syntheses.** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
 - 4. Design safer chemicals.** Chemical products should be designed to effect their desired function while minimizing their toxicity.
 - 5. Safer solvents and auxiliaries.** The use of the auxiliary substances – solvents, separation agents, and others – should be made unnecessary wherever possible and innocuous when used.
 - 6. Design for energy efficiency.** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
 - 7. Use renewable feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
 - 8. Reduced derivatives.** Unnecessary derivitization – use of blocking groups, protection/deprotection, and temperature modification of physical/chemical processes – should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
 - 9. Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
 - 10. Design for degradation.** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
 - 11. Real-time analysis for pollution prevention.** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
 - 12. Inherently safer chemistry for accident prevention.** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.
-

Source: P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.

Meanwhile, worries about the environment, the poor public image of the chemical industry, and more stringent government legislation caused concerned chemists in the 1990s to draw together under the “green chemistry” banner. Certain topics, for example, avoidance of phosgene, use of dimethyl carbonate (Sections 9.1.2.2 and 9.3.1), elimination of organic solvents, and development of reactions in supercritical carbon dioxide and ionic liquids, are particularly associated with the movement, as are biphasic systems and solvent-free systems that use as catalysts the surfaces or interiors of clays, zeolites, silica, and alumina.

Most of the modern “green” processes fall into the area of fine chemicals rather than bulk organic chemicals. Nonetheless, they have had an impact on bulk chemical processing in terms of emissions, heat conservation, and catalyst development.

Steam cracking and catalytic reforming are probably here to stay, but the earlier chapters of this book have described many biotechnological and otherwise “green” processes for medium tonnage chemicals. This chapter is a sort of addendum to the processes we have already described. By drawing together a number of unconnected green processes and trends that struck us as interesting, we hope to indicate how some of the objectives in Table 19.1 are being achieved.

19.1 THE DECLINE OF ACETYLENE CHEMISTRY

Before World War II, acetylene was the basic feedstock for many aliphatic organic chemicals, especially monomers. Production of acetylene via carbide produced about 28 metric tons of a slurry of calcium hydroxide in water for every metric ton of acetylene (Section 12.3). The process was polluting and energy intensive. The replacement of acetylene by ethylene as a feedstock made possible the modern chemical industry – it is inconceivable that its growth could have occurred with such a polluting first step. It is a matter for some regret that the Chinese have revived some of the old carbide-based processes, and the effect on their environment and general health has been poor. Acetylene’s decline in the United States is illustrated in Figure 12.1.

19.2 NYLON

The production of nylon 6 by the classical process (Section 9.2.1) produces 4.4 kg of ammonium sulfate for every kilogram of product. Processes are described in that section that decrease or eliminate ammonium sulfate production. Sumitomo brought on stream the Enichem (now Syndial) ammoximation process in 2003 in Ehime, Japan. Two processes under development by DSM and BASF also seem favorable.

The Flixborough disaster in 1974 led to a modification of the nylon 6 process in Britain in which phenol was substituted for benzene-based cyclohexane. A leak had occurred in the cyclohexane line, leading to an unconfined vapor cloud explosion that caused 28 deaths. Although the explosion was attributed to various design failures, the replacement plant started with the safer phenol (Section 9.1.3).

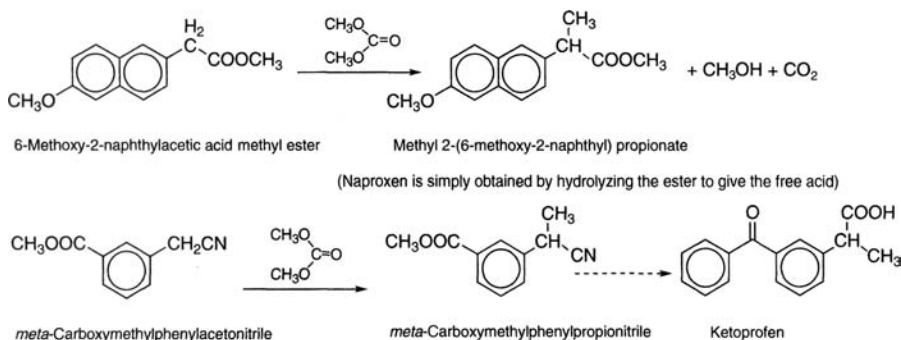
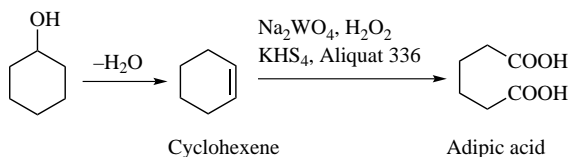
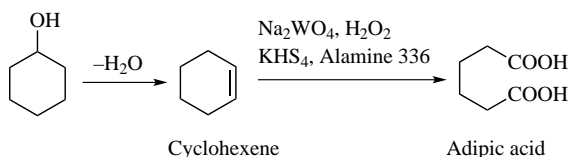


FIGURE 19.1 Methylation by dimethyl carbonate.

There are also some ecological problems associated with nylon 66 (Section 9.2.1). Adipic acid synthesis, like the traditional nylon 6 process, starts with benzene, which is toxic.¹ Mild oxidation of benzene gives a cyclohexanol/cyclohexanone mixture.



A more severe oxidation with nitric acid oxidizes this mixture to adipic acid. This is the only large scale industrial oxidation requiring this polluting reagent. BASF has developed a more benign process starting with butadiene (Section 7.1.6.4). Other processes have been proposed but not commercialized. One of these goes via cyclohexene and the phase-transfer catalyst, Alamine 336 [tri-(C₈–C₁₀)alkylamine]:



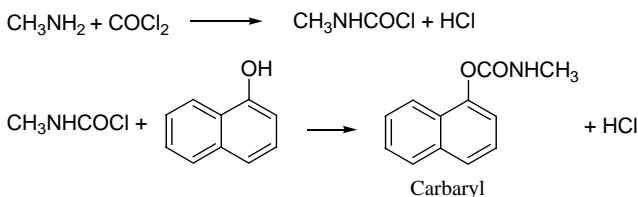
The reaction can be run in water. The Aliquat serves to transfer the oxidizing system to the organic phase or, at least, to the interfacial layer, where reaction can take place (Section 18.10). The drawbacks are first that the reaction requires expensive hydrogen peroxide and second that the phenol starting material is more expensive than benzene. However, a Japanese process (Section 9.1.3) hydrogenates benzene to cyclohexene in good yield. A cheaper process for hydrogen peroxide would make this process more favorable.

19.3 REPLACEMENT OF PHOSGENE

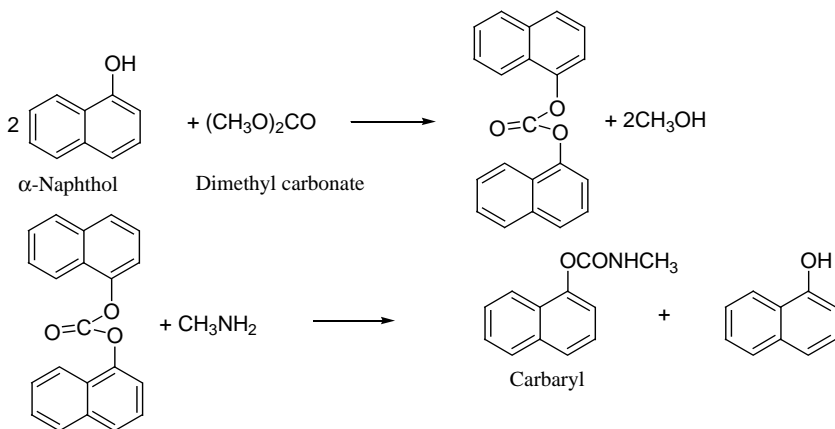
A central aim of green chemists is the development of reaction routes that do not involve the use of phosgene. A nonphosgene route to polycarbonate resins² is described in Section 9.1.2.2 and nonphosgene routes to diphenylmethane diisocyanate (MDI) and to isophorone diisocyanate are described in Section 9.3.1. By the early 2000s, only isophorone diisocyanate was manufactured without phosgene. The process used here is not applicable to aromatic isocyanates and has not been applied to other aliphatic isocyanates.

The use of phosgene was also associated with but not directly implicated in the Bhopal disaster, the worst in the history of the chemical industry. As indicated in Section 12.5.2.6, phosgene was reacted with methylamine to methyl isocyanate, which was stored and later reacted with α -naphthol to give the pesticide carbaryl. The disaster could have partly been averted by the maintenance of a much smaller inventory of methyl isocyanate, the agent that poisoned so many people. Makhteshim,

in Israel, avoided the use of the deadly methyl isocyanate but not the use of phosgene by the reaction sequence:



The pesticide could probably be made via dimethyl carbonate by the reactions:



19.4 MONOMETHYLATION BY DIMETHYL CARBONATE

Apart from its role in replacing phosgene (see above), dimethyl carbonate is a “green” methylating agent and, in some reactions, it can replace dimethyl sulfate, methyl chloride, or sodium hydride.³ Two examples that have been commercialized are in the syntheses of the nonsteroidal anti-inflammatory drugs ketoprofen and naproxen. In both cases, insertion of a methyl group alpha to a carboxyl is required. The crucial stages are shown in Figure 19.1. Dimethyl carbonate is a methylating agent only at high temperatures and boils at 90°C, so reactions must be carried out in an autoclave. Because it is harmless, it can be used in large excess and can serve as a solvent at the same time as a methylating agent.

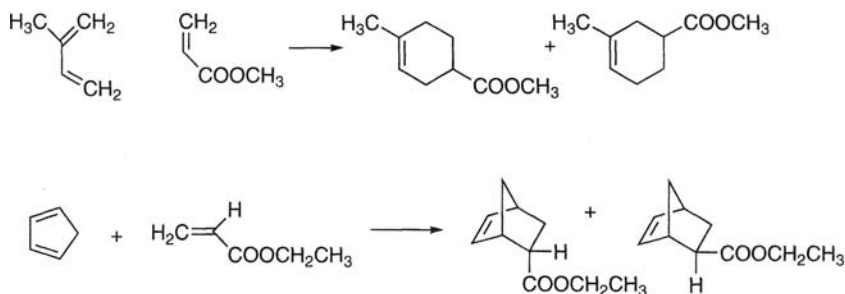
19.5 LIQUID AND SUPERCRITICAL CARBON DIOXIDE AND WATER

Carbon dioxide has a triple point, the conditions under which solid, liquid, and vapor can exist together in equilibrium, of -56.6°C and 5.2 bar. When cooled at atmospheric

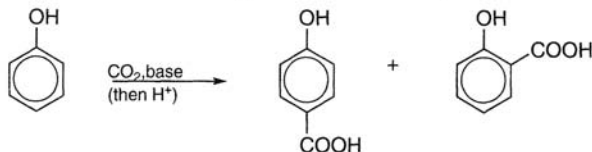
pressure, it condenses directly to a solid – dry ice. When compressed at room temperature it liquefies and is often supplied commercially in cylinders as a liquid exerting a pressure of 56.5 bar. When compressed above its critical point (31.1°C) it gives a supercritical fluid. The potential use of liquid carbon dioxide as a replacement for tetrachloroethylene (perchloroethylene) in dry cleaning was mentioned in Section 5.11.7. Supercritical carbon dioxide is used instead of hexane to extract caffeine to give decaffeinated coffee: it is forced through the green coffee beans, and then they are sprayed with water at high pressure to remove the caffeine. Supercritical carbon dioxide is also used to extract vegetable oils and perfumery oils from their substrates. The advantage in the cases of caffeine and vegetable oils is that there is no contamination issue. The perfumes undergo less decomposition and have cleaner “notes.”

Reactions normally carried out in chlorofluorocarbon solvents have been found to proceed in liquid or supercritical carbon dioxide. DuPont announced in 2000 a plant to make polytetrafluoroethylene and its copolymers by such a process using fluorinated initiators. Thomas Swan, in England, opened a plant in 2002 to hydrogenate isophorone to trimethylcyclohexanone.⁴ Figure 19.2 shows various other reactions demonstrated to take place satisfactorily in supercritical carbon dioxide, some of which might find application in industrial processes.⁵ Liquid carbon dioxide is also a

Diels–Alder reactions



Kolbe–Schmidt reaction (Marasse modification)



Friedel–Crafts reaction

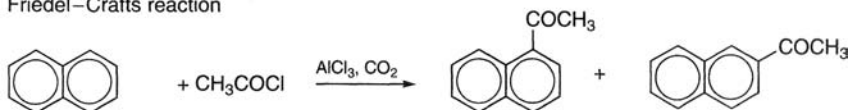


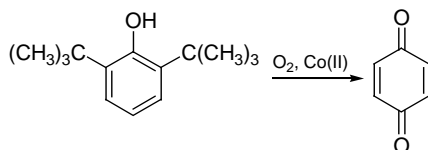
FIGURE 19.2 Some reactions occurring satisfactorily in supercritical carbon dioxide.

replacement for chlorofluorocarbons and other organic solvents in cleaning integrated circuits and other microelectronics components.

Supercritical carbon dioxide has a chemical application when applied to fully hardened hydraulic cement or gypsum plaster. It reacts with the alkaline components of these materials to give various carbonates, which can replace more expensive ceramics.⁶

Supercritical carbon dioxide is also used in the foaming of polymers. Many corporations utilize supercritical carbon dioxide to saturate the polymer with solvent (carbon dioxide). Upon depressurization and heating the carbon dioxide rapidly expands, causing voids within the polymer matrix, that is, creating a foam.

An advantage of liquid or supercritical carbon dioxide is that a large degree of control over product selectivity and yield is possible by adjusting the temperature and pressure of the reactor. Supercritical fluids also allow easy recovery of the product and separation of the catalyst. There are, however, several drawbacks. First, the achievement of high pressures is expensive and offends one of the “green” commandments. Second, pure supercritical carbon dioxide frequently leads to low reaction rates and inadequate catalyst solubilities. The latter problem has led to the idea of a “CO₂-expanded” solvent, that is, a mixture of an organic solvent with the carbon dioxide. For example, 2,6-di-*tert*-butylphenol in acetonitrile may be oxidized to 1,4-benzoquinone in acetonitrile/supercritical CO₂ in a 1:1 ratio with a cobalt(II) catalyst.⁷



Carbon dioxide increases the solubility of oxygen by nearly two orders of magnitude compared with pure acetonitrile, while the acetonitrile aids catalyst solubility and allows a rapid catalyst turnover rate. The system will operate at 60–90 bar compared with the 200 bar required for pure supercritical carbon dioxide, and the catalyst can be recovered simply by increasing the carbon dioxide pressure until the catalyst precipitates. Although the technique is ingenious, the question arises as to whether it could be applied to commercially more important systems.

19.6 IONIC LIQUIDS

Ionic liquids are salts of nitrogen- or phosphorus-containing organic cations coupled with inorganic anions. Because of the asymmetry of the cations and size differences between them and the anions, they do not pack readily into a crystal and consequently are liquids at room temperature. Typical ionic liquids are shown in Figure 19.3.

The cations and anions can be varied to give different degrees of lipophilicity and hence different solvating properties. They are usually air and water stable.

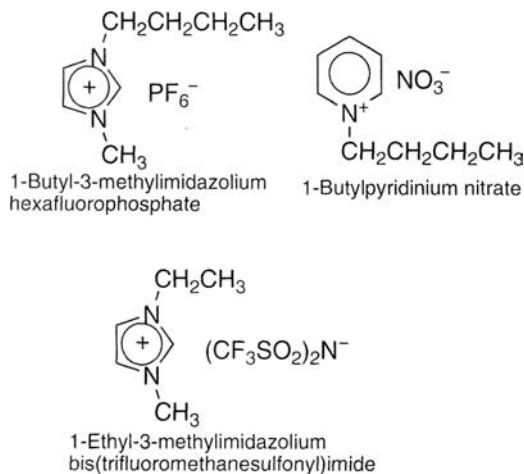
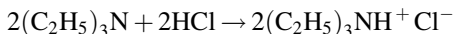
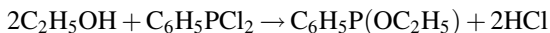


FIGURE 19.3 Ionic liquids.

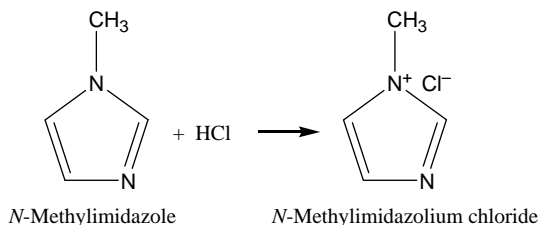
They consist mainly of discrete dissociated ions or as strongly structured liquids, with the electric conductivity of salts. They have practically zero vapor pressures, which means that in terms of emissions they are ideal replacements for volatile organic solvents. The downside is that they themselves cannot be purified by distillation. There is also a possible problem in that ionic liquids are usually lipophilic and, as noted above, lipophiles accumulate in body fat and are not regarded as environmentally friendly. The reaction products in ionic liquids can either be distilled off or extracted with water or alkanes.

The largest plant to date using ionic liquids is Petrochina's 65,000 metric ton/year plant for alkylating isobutane with isobutene to give gasoline. Instead of a hydrofluoric or sulfuric acid catalyst, Petrochina uses an ionic liquid based on aluminum chloride.⁸

BASF was a pioneer of ionic liquids when it introduced the BASIL (Biphasic Acid Scavenging utilizing Ionic Liquids) process.⁹ The synthesis of alkoxyphenylphosphines, which are precursors in the synthesis of photoinitiators used in ultraviolet-light-curable coatings, generated hydrochloric acid. This was conventionally scavenged by triethylamine:



The triethylammonium chloride that resulted formed an insoluble paste that was difficult to handle. Replacement of triethylamine by *N*-methylimidazole gave the ionic liquid *N*-methylimidazolium chloride, which partitions the reaction mixture into two phases so that the product could be isolated.

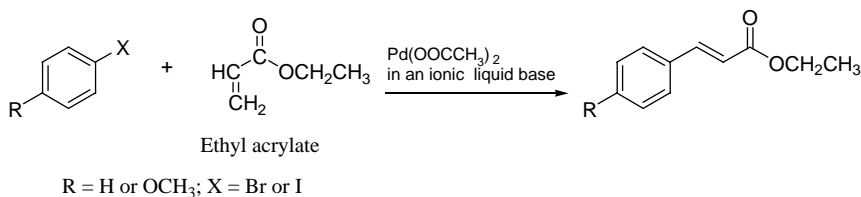


The *N*-methylimidazole could simply be recovered by washing the ionic liquid layer with sodium hydroxide solution. The ionic liquid system increased yields from 50% to 98% and turnover increased 86,000 times.

Another process employing ionic liquids is the Difasol modification to the Dimersol process (Sections 6.3 and 7.3). The Dimersol process is widely used in the dimerization of alkenes to branched chain hexenes and octenes. The process is normally run solvent-free and uses a nickel-based catalyst of the form $[(\text{PR}_3)\text{NiCH}_2\text{R}'][\text{AlCl}_4]$. Separation of the catalyst from the products, however, is a major problem. Immobilization of the nickel catalyst in an ionic liquid phase permits easy product/catalyst separation and enhances the activity of the catalyst. A similar idea is used in the carbonylation of methanol to acetic acid (Section 12.5.2.2), where Eastman is developing a process in which the rhodium catalyst is immobilized in an ionic liquid. It operated an ionic liquid-based plant for the synthesis of 2,5-dihydrofuran from 1996 to 2004.

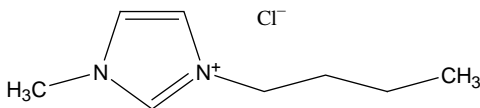
Evonik uses ionic liquids as solvents to functionalize polysiloxanes. Siloxanes are modified with polyether, alkyl, and aryl groups to give polyethersiloxanes, which are used as stabilizers and cell openers in polyurethane foams and as antifoams, emulsifiers, wetting agents, and dispersants. The snag was that the expensive homogeneous platinum or rhodium catalyst that facilitates the hydrosilylation reactions is not recycled during the standard process. Evonik devised a solution in which the catalyst is immobilized in an ionic liquid. When the hydrosilylation reaction is complete, the functionalized siloxane can be phase-separated, and the ionic liquid and catalyst can be recycled a number of times without the need for further purification.

Evonik is using ionic liquids as dispersants for colors in paints and as electrolytes in lithium-ion batteries. BP was said in 2001 to be on the point of using ionic-liquid Friedel–Crafts alkylation technology to upgrade an existing process, but little has been heard of it since. The technology apparently applies to the Heck reaction:



Another application, still some distance from commercialization, is the replacement of carbon disulfide as a solvent for cellulose (Section 16.4). A group at the

University of Alabama has found that cellulose from virtually any source (fibrous, amorphous, pulp, cotton, bacterial, filter paper, etc.) can be dissolved readily and rapidly, without derivatization, in a low-melting ionic liquid, 1-butyl-3-methylimidazolium chloride, by gentle heating, especially with microwaves. The dissolved cellulose can be reconstituted in water as fibers, membranes, or beads by conventional extrusion spinning or forming techniques.¹⁰



1-Butyl-3-methylimidazolium chloride

19.7 PHOTOCATALYSTS

There has been a feeling for many decades that there should be some way of using light instead of heat to activate molecules and bring about selective reactions – a sort of industrial flash photolysis. The Toray process to caprolactam, however, is one of the very few to be commercialized (Section 9.2.2). One of the difficulties is to get the light energy very far into the reacting system before it is absorbed and degraded by heat, chemical absorbers, and turbidity.

There is, however, research interest in the use of ultraviolet light in water purification. One of the problems with paper recycling and water purification generally is that it involves chlorination. This has the desired effect of bleaching the pulp in the first case and killing bacteria in the second, but it also results in the appearance of tiny quantities of organochlorine impurities in the wastewater, and these add to organochlorine compounds from agrochemicals.¹¹ Thus wastewater contains tiny quantities of chlorophenols, dioxins, and polychlorobenzenes. Such chlorinated compounds are anathema because, although present in minuscule quantities, they are lipophilic and accumulate in body fat.

A possible solution is to irradiate the water with ultraviolet light over a titanium dioxide photocatalyst, perhaps loaded with platinum. Water is transparent to ultraviolet light. The photoreaction on the titanium dioxide yields hydroxyl ions, which displace the chlorine atoms on the aromatic rings. The mechanism by which the aromatic rings are fragmented is unclear, but it is known that the catalyst system yields hydrogen and oxygen from water but with very low quantum efficiency. The end products are certainly carbon dioxide, water, and hydrogen chloride which, at the level at which it is formed, is harmless.

Water purification illustrates some of the dilemmas facing the green chemist. It is essentially an end-of-pipe process, which is against the general principle (Table 19.1). One way of reducing the organochlorine compounds would be to reduce paper recycling, but recycling is a cardinal principle of greenness. A cheap route to hydrogen peroxide would provide a worthwhile series of alternative technologies,

and it will be interesting to see if Solvay's approach (Section 9.8.1) will turn out to be widely applicable.

19.8 PAIRED ELECTROSYNTHESIS

In the late 1990s, BASF developed a two-for-one electrochemical process to produce two complex chemicals – phthalide and *tert*-butylbenzaldehyde (TBA) – both of them intermediates in BASF's crop protection products.¹² The reaction sequences are shown in Figure 19.4. BASF's original process for manufacture of TBA involved alkylation of toluene with isobutene to give *para*-methyl-*tert*-butylbenzene, and this was oxidized in an electrochemical reactor to give TBA dimethyl acetal, the precursor of TBA, at the anode and hydrogen at the cathode. The hydrogen was impure and had to be burned. On hydrolysis, the acetal loses methanol to give TBA.

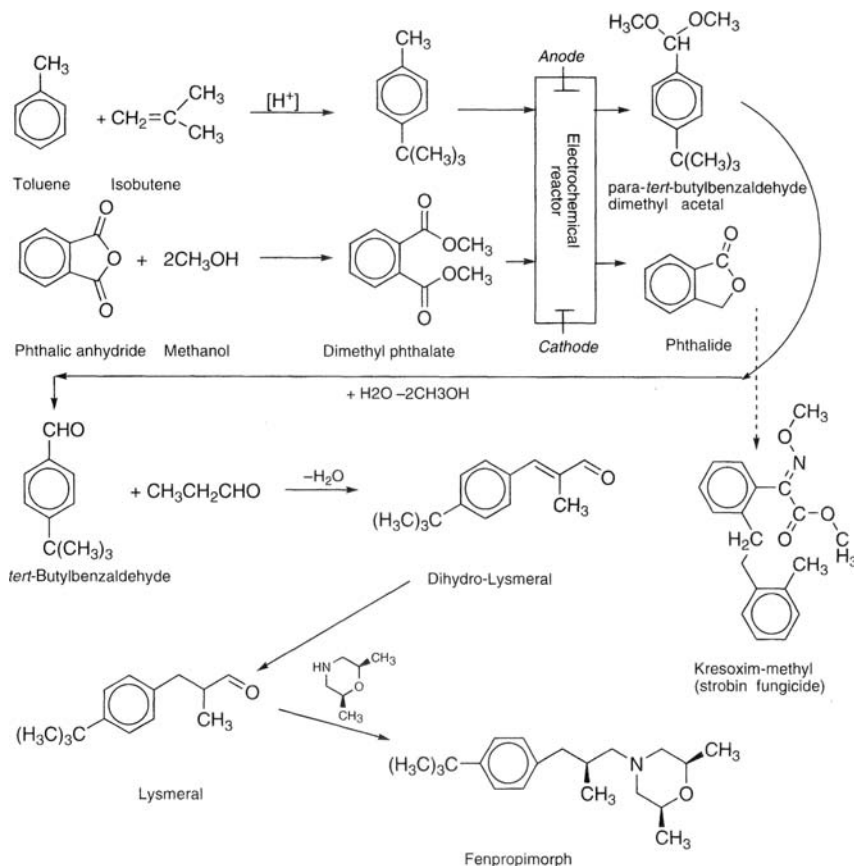


FIGURE 19.4 Paired electrosynthesis of phthalide and *tert*-butylbenzaldehyde.

When phthalide was required as an intermediate, BASF realized that the electrochemical reactor could be set up to give phthalide simultaneously from the dimethyl phthalate at the anode. Phthalide is an intermediate for the relatively new, “green” fungicide kresoxim-methyl. The TBA was reacted with propionaldehyde in an aldol condensation to give dihydro-Lysmeral. Regioselective hydrogenation of the double bond in the dihydro-Lysmeral gave Lysmeral, an aroma chemical with a lily-of-the valley fragrance. Reductive amination of Lysmeral with 2,6-dimethyl-morpholine gives the agrochemical fenpropimorph. The plant has a modular construction so that, if demand for phthalide is insufficient, TBA can be produced alone as it used to be.

19.9 “GREEN” PHARMACEUTICALS

The commandments of green industrial chemicals change somewhat in emphasis when applied to pharmaceuticals. These are generally outside the scope of this book, but a few examples are worthy of notice. Pharmaceuticals may be made synthetically from conventional industrial chemicals or they may be based on natural renewable sources. Ibuprofen and sertraline are examples of the petrochemical class. The natural renewable class includes products directly extracted from vegetable sources, for example, digoxin, and others made by fermentation and perhaps chemically modified, such as amoxicillin.

19.9.1 Ibuprofen

Ibuprofen is made from propylene and toluene to give isobutylbenzene (Section 18.4) but *n*-butylbenzene and 2-methyl indane are appreciable by-products. There are many syntheses, but most are based on isobutylbenzene (Section 16.4). The original synthesis was developed by Boots, a UK high-street pharmacist, in the 1960s and is shown in Figure 19.5.

The synthesis involves seven stages, with less than 100% yields at each stage, which when multiplied together gave a low overall yield and contributed to the effluent problem. In addition, the use of acetic anhydride produced a molecule of acetic acid as by-product, and the sodium ethoxide, ethyl chloroacetate, and hydroxylamine do not appear in the final product. The Royal Society of Chemistry estimated that, for every 206 kg of ibuprofen, 308.5 kg of other products emerge as waste even at 100% yields. In addition, the aluminum chloride catalyst in the set ablation process is not a true catalyst and emerges in a hydrated form that must be discarded.¹³ With the expiry of the ibuprofen patents in the 1980s, a new company BHC emerged with a “green” process shown in Figure 19.6.

The first two stages are similar to the Boots process, except that the acetylation is carried out with an HF catalyst instead of aluminum chloride. This is a true catalyst and can be recovered and reused. The acetophenone derivative is then reduced to a secondary alcohol with Raney nickel, and this is treated with carbon monoxide and

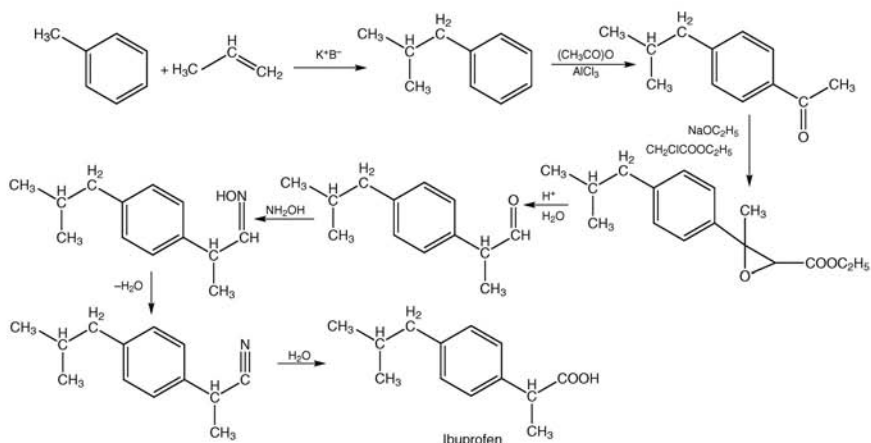


FIGURE 19.5 Boots synthesis of ibuprofen.

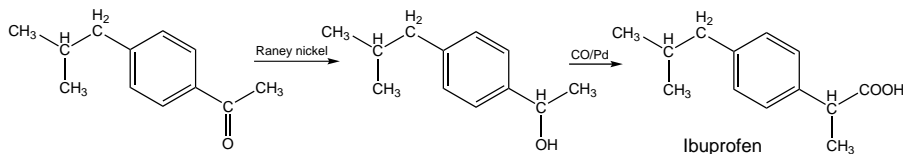


FIGURE 19.6 A “green” route to ibuprofen.

palladium to give ibuprofen. The new route has three fewer stages than the older one; the catalysts are all recoverable, and every 206 kg of ibuprofen leads only to 60 kg of by-product acetic acid. Given that the market for ibuprofen is on the order of 3000 metric tons per year in the United Kingdom alone, the worldwide savings in effluent are considerable.

19.9.2 Sertraline

Another chemically based synthesis that has become greener is that of sertraline.¹⁴ Sertraline is a pharmaceutical used to treat depression. Three steps in the original process were reduced to one (Fig. 19.7). In the original synthesis, 3,4-dichlorobenzoyl chloride and benzene were converted to a benzophenone by a Friedel–Crafts catalyst. This was originally aluminum chloride and it is not disclosed if it has been replaced by a zeolite. A side chain was built onto the ketone group and cyclized, again in a Friedel–Crafts reaction, to give (±)-4-(3,4-dichlorophenyl)-3,4-dihydro-1(2H)-naphthalenone. Three stages, later converted to one, followed. The carbonyl group of the naphthalenone was converted to an imine with methylamine in tetrahydrofuran or toluene. Titanium tetrachloride was used as a dehydrating agent to drive the equilibrium toward the imine. The imine was isolated and hydrogenated with hydrogen and a palladium/carbon catalyst in tetrahydrofuran to form isomers (*cis:trans*, 6:1). Fractional crystallization isolated the racemic *cis* hydrochloride. This was finally resolved with D-mandelic acid in ethanol to give the desired (*S,S*)-*cis* isomer. The sertraline mandelate was then converted to the hydrochloride in ethyl acetate.

In the new process, the three stages starting with the naphthalenone are carried out in ethanol without isolating the intermediates. Only the environmentally benign ethanol is used as solvent throughout and the unreacted methylamine is recovered by distillation. Titanium tetrachloride is no longer required to drive the first step since the imine is poorly soluble in ethanol and precipitates. Palladium on calcium carbonate provides better selectivity than palladium/carbon giving a *cis:trans* isomer ratio of 18:1. Overall yield has been nearly doubled to 37% and raw material usages for methylamine, (±)-4-(3,4-dichlorophenyl)-3,4-dihydro-1(2H)-naphthalenone and D-mandelic acid have been cut by 60%, 45% and 20%, respectively. Solvent requirements have been reduced from 60,000 gallons to 6000 gallons per metric ton of sertraline. Thus 440 metric tons/year of titanium

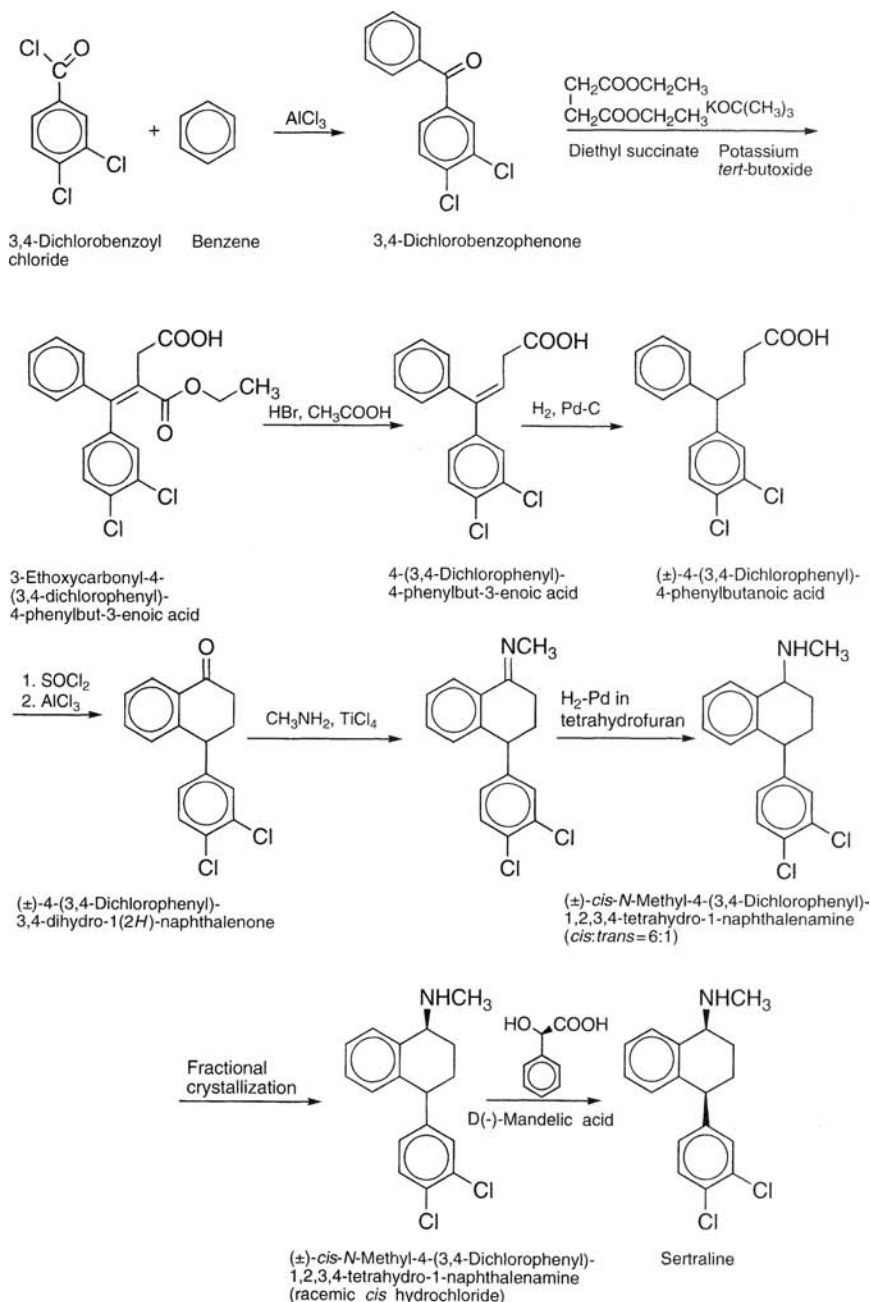


FIGURE 19.7 Synthesis of sertraline.

dioxide–methylamine hydrochloride acid waste, 150 metric tons of 35% hydrochloric acid waste, and 100 metric tons of 50% sodium hydroxide waste have been eliminated. It is to be hoped that many more examples like this will accumulate in the next decade.

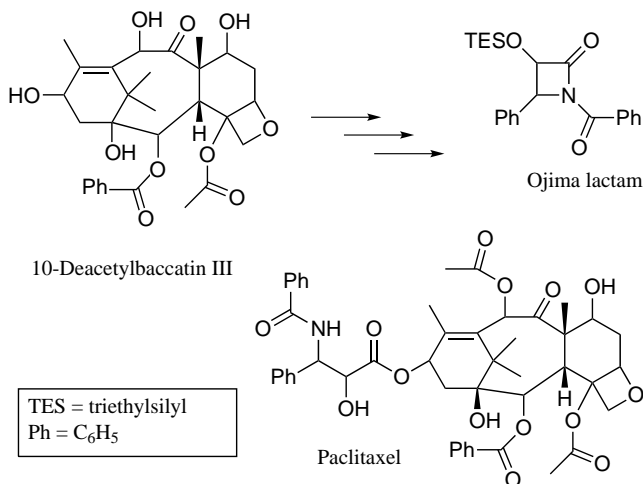
19.9.3 Pharmaceuticals from “Renewables”

The other group of pharmaceuticals where greener methods are sought are those based on naturally occurring renewable raw materials. A drug such as digoxin, which is extracted from the white foxglove, *Digitalis lanata*, is produced simply by an extraction process, but it occurs as a mixture with other cardiac glycosides, which are wasted. Boehringer Mannheim in Germany developed a method of converting one of them, digitoxin, to digoxin by means of a plant cell culture. In the living plant, digitoxin is the precursor of digoxin and undergoes 12 β -hydroxylation in certain cells to give digoxin. Boehringer Mannheim identified the cells in *Digitalis lanata* that contain the appropriate enzyme and carry out the conversion with immobilized cultures of it.

Other drugs in this class are produced by fermentation or by chemical modification of a substance occurring naturally or obtained by fermentation. An interesting example here is paclitaxel, the active ingredient in the anticancer drug Taxol. Paclitaxel was first isolated and identified in the bark of the Pacific yew tree *Taxus brevifolia*. It turned out to be useful in the treatment of ovarian cancer, but the problem was that yew bark contains only about 0.0004% paclitaxel. The production process requires stripping the bark from the yew trees, which kills them. As yew trees take about 200 years to mature, the production of commercial quantities of this drug could have rendered the species extinct.

The first move toward a sustainable supply was the development by Bristol-Myers Squibb of a semisynthetic route based on 10-deacetylbaccatin III (10-DAB), which is present at the 0.1% level in the leaves and twigs of the European yew, *Taxus baccata*, and it can be isolated without harm to the trees. The free hydroxyl group of the 10-DAB is linked to the so-called Ojima lactams, which is made by an asymmetric synthesis via a chiral auxiliary.¹⁵ While the new process was viable, it still led to effluent from the lactam manufacture and large amounts of waste biomass from the residual leaves and twigs.

Bristol-Myers Squibb therefore turned to plant cell technology. In the cell fermentation stage of the process, calluses of a specific *Taxus* cell line are propagated in a wholly aqueous medium in large fermentation tanks under controlled conditions at ambient temperature and pressure. The feedstock is sugars, amino acids, vitamins, and trace elements. The paclitaxel is extracted from the plant cell cultures, purified by chromatography, and isolated by crystallization. Compared with the semisynthetic route, the plant cell culture eliminated an estimated 32 metric tons of hazardous chemicals and other materials, 10 solvents, six drying steps, and much energy. It also allows year-round harvest and eliminates the solid biomass waste.



The "green" route to paclitaxel not only ticks the boxes of the Green Commandments, but also makes a life-saving drug freely available.

Vitamin B₂ (riboflavin) is a diet supplement rather than a pharmaceutical, but we shall include it under this heading. It is used in animal nutrition and added to breakfast cereals. Until 1990, it was made by a long synthetic method. The final stages of the synthesis are shown in Figure 19.8.

BASF pioneered the biocatalyst production of riboflavin and replaced chemical synthesis by a biotechnological process in 1990. Since then, it has produced riboflavin by fermentation using the fungus *Ashbya gossypii*. The nutrients include vegetable oil. The fungus has enzymes with which it can produce vitamin B₂. How much it produces depends on the quantity of enzymes and the fungal growth conditions. BASF brought

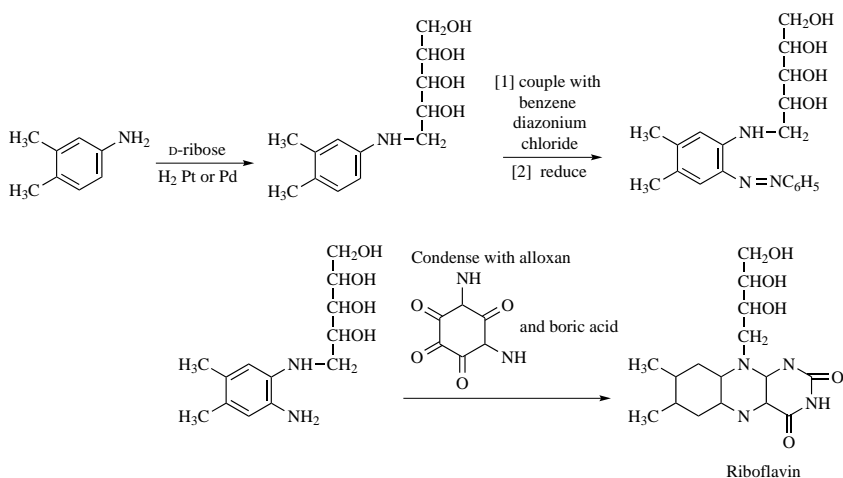
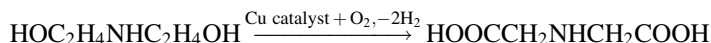


FIGURE 19.8 Industrial synthesis of riboflavin.

on stream a riboflavin plant in Gunsan, Korea, in December 2003 with a capacity of 3000 metric tons/year. BASF claims that identification of the enzymes involved in the process had reduced the resources required by 60%, carbon dioxide emissions by 30%, waste by 95%, and production costs by 40%.¹⁶

19.10 CATALYTIC DEHYDROGENATION OF DIETHANOLAMINE

The environmentally friendly nonselective herbicide Round-Up is the mono-(isopropylamine salt of glyphosate (*N*-(phosphonomethyl)glycine; $\text{HOOCCH}_2\text{NH-CH}_2\text{OP(=O)(OH)}_2$). The key intermediate in the synthesis is disodium iminodiacetate. This used to be made by the traditional Strecker process from ammonia, formaldehyde, hydrogen cyanide, and hydrochloric acid, but the process produced 1 metric ton of cyanide and formaldehyde-containing waste for every 7 metric tons of product. The new route starts with diethanolamine (Section 5.11.6.4), which is dehydrogenated over a copper-containing catalyst.¹⁷



The reaction is endothermic, avoiding the possibility of a runaway reaction and negligible quantities of effluent are produced.

19.11 GENETIC MANIPULATION

Biotechnology has been a buzzword among chemists for at least two decades as a way of using renewable raw materials and producing biodegradable products. Over that period, with the aid of recombinant DNA technology, it has led to the development of the order of 50 pharmaceuticals, but tonnage products have been lacking. There is an economic problem in harvesting natural products rather than pumping them out of the ground, and there is a waste disposal problem in getting rid of the huge amounts of biomass that accompany the biotechnological product. The production of fermentation ethanol was discussed in Sections 4.15.1, 5.9, and 16.6.5. Immobilized enzyme production of high fructose corn syrup is discussed in Section 16.1 and that of acrylamide in Section 6.11.3. Use of engineered enzymes is a route to 1,3-propanediol (Section 18.8) and many other chemicals.

19.12 BIODEGRADABLE PACKAGING

The original semisynthetic polymers – the cellulose – were based on renewable raw materials and would biodegrade.¹⁸ Polymers made from petrochemicals, by contrast, biodegrade very slowly; hence plastic waste presents problems of disposal. Discarded

plastics are a major cause of pollution, cluttering rivers, seas, beaches, and countryside, killing fish, choking birds, and making cities less attractive. In the United States only 7% by weight of the contents of waste dumps is plastics, but that still amounts to 20% by volume. Forty percent of the litter along roadsides is plastics, and this visibility, abetted by consumer concern, has motivated the development of photodegradable plastics. These were already in use in the early 1990s for yolks for “six-pack” beverage bottles in those states where legislation required it. There was evidence that animals were trapped by the holes in these yokes.

The number of discarded artifacts is incredible. The world used about 500 billion plastic bags in 2008, 4.5 per man, woman, and child. The United States used 100 billion of these, about 330 per person and the British about 8 billion, about 133 per person. It is claimed that the average bag is used for 12 minutes and takes 500 years to break down in the tip (but there is evidence that they help to stabilize tips – life is never straightforward!). The requirements for “useful” biodegradability are recognized in various ASTM documents.¹⁹

The production of biodegradable polymers is of increasing interest. A distinction must be drawn between three classes of biopolymers:

- Those that are made from renewable raw materials but are not biodegradable, such as biopolyethylene made from fermentation alcohol
- Those that are based on petrochemicals but are biodegradable, such as the polyolefins containing photosensitive groups (see below)
- Polymers that are both made from renewable raw materials and are also biodegradable, such as the polyhydroxyalkanoates (Section 19.12.1)

Figure 19.9 shows the 2010 global capacities for biopolymers and the predictions for 2015.²⁰ Starch-based polymers and cellulose are not predicted to expand greatly. Biopolyethylene, polylactic acid, and polyesters of various kinds are where the interest seems to lie.

Many of the early biodegradable plastics were based on starch. The first generation bags consisted of 80–95% polyethylene or polypropylene, with starch merely acting as a filler. After disposal, the starch degrades and a residue of small nonbiodegradable particles is left, which remain invisibly in the environment.

Starch is used for its polymeric properties in the second generation of degradable plastics. It is blended with a hydrophilic synthetic polymer, typically poly(vinyl alcohol), and contributes to the strength of the material. Fifty to eighty percent starch can be used in these plastics, but the remainder is not biodegradable.

The third generation of materials are truly biodegradable and do not contain petrochemicals at all.²¹ The main group is the polyalkanoates (see below). We stress that biodegradability is not the only issue, and that the barrier properties of films made from these different materials dictate the uses. Packaging of fruit and vegetables requires film reasonably permeable to oxygen and/or carbon dioxide. Foods sensitive to oxygen, for example, those containing polyunsaturated fats, which can go rancid, require very low oxygen permeability. And many other storage characteristics such as

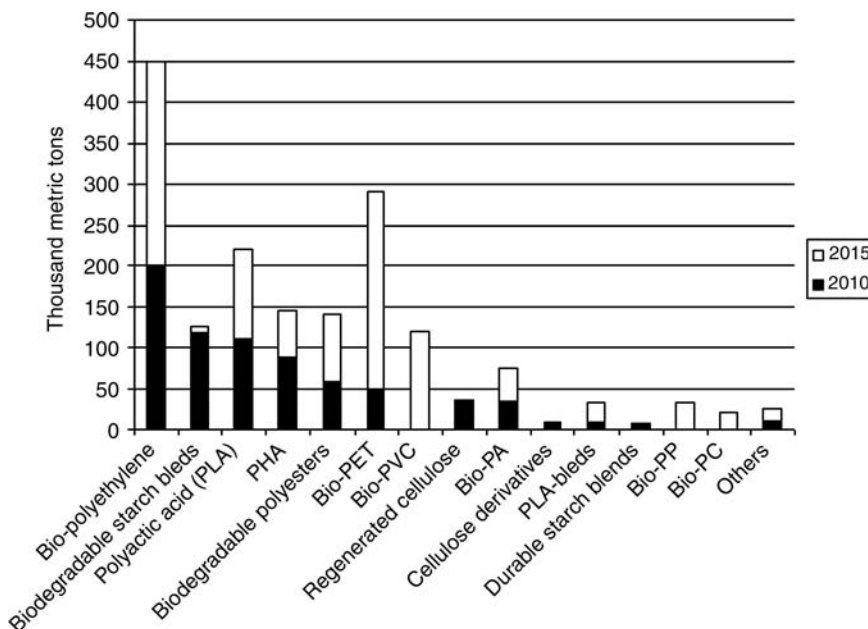


FIGURE 19.9 Biopolymer production capacity, global 2010 and 2015. (Source: Based on European Bioplastics University of Applied Sciences and Arts, Hanover.)

microbial growth, chemical reactions, and crispness depend on permeability to water. Table 19.2 shows the properties of some biodegradable films.

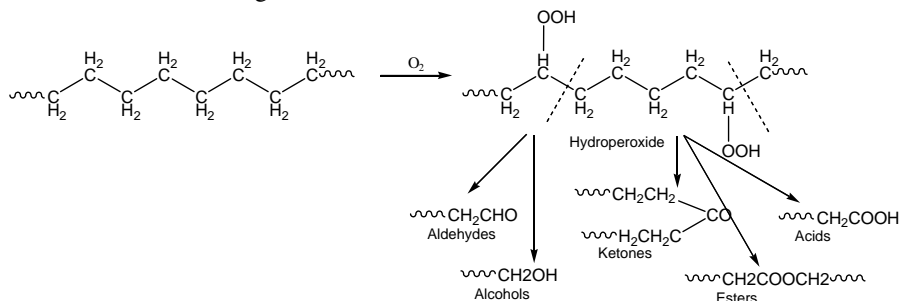
The persistence of conventional petrochemical polymers in the environment is of concern, but it is significant that they eventually photo- and biodegrade. This occurs in two stages. The key intermediates are hydroperoxides that decompose under the influence of heat, light, and catalysts to produce free radicals. These promote chain

TABLE 19.2 Properties of Some Biodegradable Films

Material	Moisture Barrier	Oxygen Barrier	Mechanical Properties
Cellophane	+ / -	+	+
Cellophane coated with nitrocellulose-wax	+	+	+
Cellulose acetate	+ / -		+ / -
Starch/polyvinyl alcohol	-	+	+
PHB/polyhydroxybutyrate/valerate	+	+	+ / -
Polylactic acid	+ / -	-	+

Sources: Wageningen University University for Life Sciences, Department of Agrotechnology and Food Sciences. Processing of Agricultural Raw Materials for Non-Food Products. P050-217. <http://www.ftns.wau.nl/agridata/historybiodegrplast.htm>27oct01; <http://www.mindfully.org/Plastic/Biodegradable-Plastic.htm>.

reaction and loss of molecular mass giving aldehydes, alcohols, ketones, esters, acids, and low molecular weight waxes.



The oxidation stage reduces the hydrophobicity of the polymer and this makes biodegradation possible. Cell enzymes, particularly cytochrome P450 which is produced by many bacteria, continue peroxidation and polymer fragmentation. Bioassimilation to biomass, water, and CO_2 continue as long as environmental oxygen and cell nutrients are available.

This is a very slow process, but the polymers can be rendered more biodegradable by the introduction into the polymer chains of photosensitive $>\text{C}=\text{O}$ groups. The polymer is reacted with a compound such as NOCl in the heterogeneous phase in an acid environment so that $-\text{NO}$ groups are introduced into the polymer chain, that are converted into $>\text{N}-\text{OH}$ groups. The resultant polymer is then hydrolyzed so that the $>\text{N}-\text{OH}$ groups are converted into photosensitive $>\text{C}=\text{O}$ groups. These keto groups absorb UV radiation and cause photodegradation of the polymer. There are certain proprietary additives, the best known of which is TDPA (totally degradable plastic additive) that have a similar action.²² Other photosensitizers include diketones and aminoalkylferrocenes.

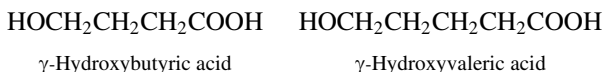
The techniques are applied to such polymers as polyethylene, polypropylene, and polystyrene. They photodegrade on exposure to direct sunlight, but have indefinite storage life otherwise. The level of photosensitive groups is typically designed to provide a useful lifetime of about 6 months under normal conditions. Six-pack soda can rings and yokes for beverage bottles have been made of photodegradable LDPE since the 1990s in those states where legislation required it. There was evidence that animals were trapped by the holes in these yokes.

An example of a photodegradable polymer was a product containing ethylene, propylene, and carbon monoxide, developed by Shell and BP but subsequently dropped. It was an alternating copolymer of structure $[-\text{CH}_2\text{CH}_2\text{COCH}_2(\text{CH}_3)\text{CH}_2\text{CO}-]_m$. The ketone group contributed the photodegradability. The homogeneous copolymerization is carried out with a catalyst comprising a palladium salt of trifluoroacetic acid with *para*-toluenesulfonic acid with a bidentate ligand identified in the patent literature as 2,2'-bipyridine 1,10-phenanthroline or 1,3-bis(diphenylphosphino)propane.

19.12.1 Polyhydroxyalkanoates

The polyhydroxyalkanoates are more tractable than the celluloseics but are still based on renewable raw materials (Sections 16.1 and 16.6.2). Initially ICI developed a route

to a biodegradable polyester copolymer of γ -hydroxybutyric and γ -hydroxyvaleric acids, by fermentation of glucose with *Alcaligenes eutrophus*.



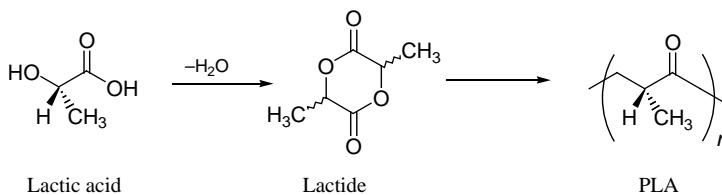
The polymer, called Biopol, is stereoregular and has a molecular weight of 100,000 to 400,000. After separation from microbial cells and purification, it can be formed by conventional polymer processing techniques. The stereospecificity and high molecular weight, which give it strength, are unique for step growth polymerization which, when performed conventionally, gives molecular weights as low as 10,000. The polymer, *polyhydroxybutyrate*, is still expensive but its biodegradability makes it attractive and it is finding a market in the blow-molding of bottles and other packages, particularly for “green” cosmetics. It was sold to Monsanto which sold it to Metabolix, which has developed recombinant organisms that are much more efficient than the wild strains used by Monsanto. The process uses renewable feedstocks, such as cornstarch, cane sugar, cellulose hydrolysate, and vegetable oils. Metabolix is also developing crop plants such as tobacco or rapeseed that could grow Biopol and other polyhydroxyalkanoates directly.²³

Biopol is already used for sutures, and other medical applications such as staples, ocular inserts, cardiovascular grafts, and bone screws, and related surgical items are planned. Because the polymer is biodegradable, postsurgical removal is not required. Also, because of its biodegradability, the polymer might be useful in controlled release of drugs, applicators for feminine hygiene products, for the encapsulation of pheromones, and for agricultural film in which fertilizers and insecticides are imbedded. A decreased price would make it a candidate for general purpose biodegradable film.

A related polyalkanoate is polylactide (polylactic acid, PLA), a polyester from lactic acid.²⁴ Cargill Dow opened a 140,000 metric ton/year plant in 2002, based on an engineered organism, and aimed at a global capacity of 500,000 metric tons/year by 2010. Coca-Cola used **50,0000** polylactide cups in the Winter Olympics in Salt Lake City, but we have not seen an announcement of the new plant. A drawback is that lactic acid needs to be polymerized to give polylactide, whereas Biopol is produced ready-polymerized by the organism. A South Korean group has claimed to have genetically modified an *E. coli* organism to give polylactide and its copolymers directly.²⁵

In the Cargill Dow process, dextrose from corn is first fermented to lactic acid by a route similar to that in Section 16.1. The lactic acid is purified and condensed to make low molecular weight polylactic acid ($M_n \sim 5000$). This is then depolymerized in the melt with a tin octanoate catalyst to give a mixture of lactide stereoisomers. Traces of water formed in the condensation polymerization need to be removed because they limit molecular weight, and operation in the melt makes this easier than in solvents. The purification steps allow manipulation of the stereoisomers; the L-lactide is the primary product but the physical properties of the polymer can be varied by

controlling the amount of D-lactide. The final product has a molecular weight of 60,000 to 150,000 and residual lactic acid and lactide are removed under vacuum.



Avoidance of a solvent and the use of vacuum distillation give a product claimed to be competitive with petrochemicals.

Poly lactide biodegrades in a composting facility above 60°C. It looks like polystyrene and has the stiffness and tensile strength of poly(ethylene terephthalate). Polylactide films are grease resistant and have good barrier properties, which suits them for food packaging. Like cellophane, they stay folded when twisted, making them suitable for candy wrappers, and the first commercial use has been as packing film for golf balls in Japan. The melting point of polylactide is about 170°C, but manipulation of the process to give a copolymer of L-polylactide with its D-enantiomer raises the melting point to 210°C. The copolymer is not only temperature resistant but also shatter resistant and is used in spectacle frames. Polylactide is said to bridge the gap between synthetic and natural fibers in clothing and carpeting and also to have wide applications in agriculture and gardening.

It is claimed that polylactide production would not compete seriously with food production, and 500,000 metric tons of polylactide would require less than 5% of the annual U.S. corn crop. This is all very well, but 500,000 metric tons is a drop in the ocean compared with overall plastics production, and other biopolymers and renewable sources of chemicals will also be clamoring for space.

To end this section, a word should be said in favor of the plastic bag, as opposed to the “natural” brown paper bag. Paper production consumes massive amounts of fresh water. Paper recycling contaminates water with organochlorine compounds and generates air pollutants. It takes four times as much energy to produce paper bags as it does plastic, and they degrade only slightly faster in landfills. Plastic bags are easier to store and reuse. Readers who really want to be “green” should carry their groceries home in reusable bags and do away with disposable bags altogether. But they should remember that cotton crops also require huge amounts of water, and the farms that grow them use lots of synthetic fertilizers and pesticides, so maybe a polyester bag is better or, failing that, they should take a plastic bag and reuse it.

19.13 THE PRESIDENTIAL GREEN CHEMISTRY CHALLENGE PROGRAM

Attempts by the government to encourage green technology led to the Presidential Green Chemistry Challenge Program, which started in 1995. Collectively, by 2009, these award-winning technologies had eliminated more than 1.3 billion pounds of

hazardous chemicals and solvents, saved over 42 billion gallons of water, and eliminated nearly 460 million pounds of carbon dioxide releases to air. We have quoted many of the winning procedures in this book, but complete lists will be found at the U.S. Environmental Protection Agency website, <http://www.epa.gov/gcc/>.

The above examples of green chemistry have no common theme. They comprise a series of attitudes rather than a coherent body of knowledge. One could not, for example, plan a degree course in green chemistry without having a prior requirement for a degree in chemistry. Nor are “green” routes to chemicals going to be adopted if they are economically inferior to less green routes. On the other hand, governments influenced by the green movement might well apply financial pressure to companies using less green processes, but are unlikely to do so unless alternative green routes exist. The preference for environmentally friendly routes could also influence companies in their choice of lines of research. “It is early days yet,” the green chemist might say, “and if we keep in mind the commandments in Table 19.1, then the chemical industry of the future will be far more sustainable than in the past.”

ENDNOTES

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CHAPTER 20

Sustainability

In the 1950s and 1960s, the organic chemical and pharmaceutical industries grew at an astonishing pace, twice as fast as the chemical industry in general and four times as fast as the economy as a whole. The market was flooded with new and exciting polymers that provided synthetic fibers for clothes, plastics for all sorts of household goods, together with elastomers, paints, and adhesives. In the pharmaceutical field, there was a flood of new drugs that cured traditional infectious diseases and eased the cardiovascular and psychological problems of modern life. Standards of living rose so rapidly and novel processes succeeded one another so frequently that few paused to consider possible adverse consequences of such growth.

For the pharmaceutical industry, the party came to an end with the thalidomide tragedy in 1962, in which an inadequately tested but supposedly safe sleeping pill, designed to replace the dangerous barbiturates, turned out to cause birth defects when taken by pregnant women. New regulations for drug testing and safety were swiftly implemented, and the number of chemical entities reaching the market each year more than halved.

The problems of the organic chemicals industry started perhaps 10 years later. The publication of Rachel Carson's *Silent Spring* in 1962¹ was a portent. Carson claimed that the synthetic chemicals being emitted into the environment, especially DDT, were spreading worldwide and accumulating in the body fat of species high up the food chain. Birds were being harmed, their eggshells weakened. In 1972, *The Limits to Growth* by D. H. Meadows et al. appeared.² They claimed that population, standards of living, pollution, and the consumption of nonrenewable natural resources were all linked in a fairly simple way, and all were increasing exponentially. The future could be modeled even on the relatively unsophisticated computers of the time, and the conclusion was that any limited problem one could solve was part of a larger problem one could not solve. Doom was just around the corner. Forty years on, the predictions have all been falsified, but the book was immensely influential in bringing to world notice the genuine problems of pollution and resource depletion. This was a classic example of the truth that prediction *per se* is not important; what is important is what

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action the prediction motivates. The book's message was emphasized by the *Yom Kippur* Arab–Israeli war in 1973, which highlighted the fact that about two-thirds of world long-term oil reserves are concentrated in the Middle East, in countries not noted for political stability, democratic traditions, or concern for human rights. The discovery of reserves of natural gas and oil in Russia has altered the distribution pattern but not the political worries.

During the past half century, sustainable growth has been an avowed aim of developed economies. One of the main driving forces behind chemical industry research has been green chemistry, that is, the modification of processes to produce fewer waste products and less of them, and to consume fewer resources of chemicals and energy. Meanwhile, we should recognize that sustainable growth is an oxymoron. The trees do not grow to the sky, and infinitely continuing economic and population growth is a chimera. At some stage growth must level off. Malthus, writing in 1798, thought it would happen rapidly, but he misjudged the effects of the industrial revolution, which was in its early stages when he wrote. Thus we shall talk of sustainability not sustainable growth.

We shall discuss the issues of climate change, resource depletion, energy sources, and pollution. Libraries of books have already been written on all these topics, but we shall try to summarize the nature of the problems, particularly those affecting the chemical industry. At least we can point out some of the more egregious errors found in the media. This is a limited agenda, and we are not attempting to tackle the broader environmental problems. Sadly, we have no instant solutions.

20.1 CLIMATE CHANGE

The central problem facing humanity is widely thought to be that of global warming, occurring as a result of the accumulation of anthropogenic (humanmade) carbon dioxide in the atmosphere. A sequence of reports has been produced by the Intergovernmental Panel on Climate Change (IPCC) that are the basis for most discussions.

The mechanism of global warming is supposed to be as follows. The earth is protected from ultraviolet radiation from the sun below 360 nm by the ozone layer. Longer wavelength radiation, including visible light, is transmitted through the atmosphere and degraded into heat, which is reradiated as infrared radiation. Some of this radiation is reabsorbed as heat by gases in the atmosphere, and this keeps the surface of the earth at a tolerable temperature. Arrhenius coined the term “greenhouse effect” for this phenomenon in 1896, believing mistakenly that the carbon dioxide in the atmosphere acted like the glass in a greenhouse, but the term has remained in use.

Oxygen, nitrogen, and argon are transparent to infrared radiation and ozone absorbs only slightly and at a high altitude. The principal absorbers are water and carbon dioxide. Water has two broad bands in the infrared around 3800 and 1600 cm^{-1} (2630 and 6250 nm). It is the most important absorber, and its absence is the reason why deserts with dry atmospheres are cold at night. Carbon dioxide has narrow absorption bands at 700 and 2400 cm^{-1} (14300 and 4170 nm) and is responsible for

TABLE 20.1 Relative Global Warming Efficiencies of Various Gases^a

CO ₂	CH ₄	N ₂ O	CF ₄	SF ₆
1	62	275	3200	15100

^a Based on a 20-year cycle and taken from various sources.

less warming. It has been estimated that water contributes about 33°C to the temperature at the surface of the earth, while carbon dioxide contributes about 0.5°C, which might rise several degrees depending on its concentration. Other greenhouse gases include methane, sulfur hexafluoride, nitrous oxide, CFCs, and HCFCs (Section 12.2.4). Their relative efficiencies at causing global warming are shown in Table 20.1. The value for SF₆ is the highest found.

Tetrafluoromethane and sulfur hexafluoride are being phased out. Nitrous oxide is formed naturally in thunderstorms, but there are also humanmade contributions especially from agriculture. Methane is a potential problem and has strong absorption bands around 3010 and 1300 cm⁻¹ (3320 and 7700 nm). The effect of additional greenhouse gases depends on whether they absorb in the spectral gaps between water and carbon dioxide. This is far from the whole story, however. Water vapor forms clouds, which reflect radiation from the sun and keep the earth cooler during the day. They also reflect heat from the earth and keep it warmer at night. There are equilibria in which carbon dioxide is locked up in oceans, sediments, vegetation (as organic carbon), and carbonates. Note also that the addition of carbon dioxide to global temperatures is small compared with the effect of water; hence measurements of possible global warming are the difference between two large quantities, the sort of quantity that it is difficult to estimate accurately. The situation is complex and the role of water debatable.³

Atmospheric levels of carbon dioxide in the nineteenth century in the free air of the North Atlantic region before large-scale industrialization were about 280 ppm by volume. They have since risen to 313 ppm by 1960 and 383 ppm by 2009 and are predicted, under various assumptions to rise to 540–970 ppm by 2100. Methane levels have risen since 1750 by 151% and nitrous oxide levels by 17%. Methane results from anaerobic decomposition of organic matter, notably from rice paddies, animal husbandry, and landfill emission, together with leakage from natural gas installations. The reflection of these figures on world climate is not straightforward. World temperatures increased from about 1850 onwards and reached a peak in the mid-1930s. They then declined until the mid-1970s, at which time respectable academics were publishing articles on global cooling. The reasons, apparently, were increased dust hazes over deserts and bluish-green hazes over forests, probably due to terpenes. These were reflecting incident radiation and hence lowering temperatures. There are also soot, sulfate aerosols, and soot – sulfate aerosols. Some of these have a warming, some a cooling effect, but the effect of soot in promoting warming is believed to be greater than that of methane. The rise in temperatures during the twentieth century has been 0.6 ± 0.2°C. The 1990s appear to have been the hottest decade, 1998 the hottest year, and 2001 the second hottest year since instrumental records began. The first decade of the new millennium has seen a plateau in the temperature rise or even slight cooling.

Data from tree rings, corals, and ice cores suggest, at a lower level of confidence, that the twentieth century was the warmest century in the Northern Hemisphere for the past 1000 years. In the Alps, between 230 and 650 m altitude, average snow depths have decreased by 50% from the long term trend. The Eiger and Fee glaciers in Switzerland used to reach the edges of the villages of Kleine Scheidegg and Saas Fee, respectively, but have now retreated several miles from them. The ice fields on top of Mount Kilimanjaro have shrunk by 80%. Sea levels have risen by 13 cm (5 inches) since 1972, and the projected increase in temperatures between 1990 and 2100 indicates a sea level rise of between 0.3 and 0.5 m. The predicted average temperature rise between 1990 and 2100 is estimated between 1.4°C and 5.8°C.

These estimates, however, are disputed by a small but vociferous band of climate change skeptics. They argue that the modeling process is based on dividing the world into a very large number of cubes, each cube being represented by a set of equations. Each cube is programmed to calculate effects of climate under various scenarios. But this is highly complex and there are no exact solutions: variables are “parameterized”; that is, “best guess” values are assigned and adjusted to fit the experiment. The cubes are then integrated to give a global model, again an almost insurmountable computational problem. In spite of the enormous amount of computing power used, the cubes are possibly too large to give reliable results. It appears that carbon dioxide is not rising nearly as fast as the model predicts, and there is some carbon dioxide “sink” that we don’t know about.

The skeptics dispute other global warming claims. Polar bears’ numbers in the Arctic in the 1960s were estimated (reliably?) at 6000; there are about 25,000 now, so they do not appear threatened.⁴ The Himalayan glaciers are not melting at the rate claimed in the recent reports. Leaked e-mails from the Climatic Research Unit at the University of East Anglia suggested that data at odds with the global warming case had been suppressed, and other “massaging” of the data has been alleged.⁵ Temperature measurements are challenged. One infamous weather station was located next to a waste incinerator.

These and various other factors cast doubt on the accuracy of the modeling procedures. There is an acrimonious debate between scientists with different views. Far from there being a scientific consensus on the issue, few scientists even understand the modeling process. There is little rational discussion, and the issue has become politicized to the point at which an unbiased conclusion is barely possible and certainly beyond the scope of this book. But the fact remains that the world did get dramatically warmer during the 1990s, and this was probably related to carbon dioxide and other greenhouse gas concentrations. If nothing else, the modeling has shown the complexity of the interactions and feedback loops, many unfortunately positive. The consequences of increase in temperatures could well be nonlinear and might lead to major climatic instabilities. The warming of the polar ice caps could lead to increases in atmospheric methane both from melting methane hydrate (Section 20.3.5) and from methane leakage through melting permafrost.

On the other hand, Reading University (UK) has predicted a decrease in sunspot activity that could block the winds that keep Europe from excessive cold in winter.⁶ This could lead to a series of bitterly cold winters, with average temperatures falling

by about 2°C. The earth's climatic changes are driven by macro events, and it is still uncertain what brought on the Ice Ages.

To add to the above forecasts, a nuclear war – the great concern of the cold war years – would throw dust into the upper atmosphere and could lead to a nuclear winter. Maybe this will become of concern again with the proliferation of nuclear weapons. Their acquisition by Iran, a theocratic country, will terrify not only Israel (probably already nuclear) but the Sunni Muslim countries of the Middle and Far East who might decide to follow suit.

It seems highly likely if not completely certain that climate change is related to human activity. The feeling in the 1980s was that the consequences of getting it wrong were so serious that greenhouse gas levels should at least be stabilized. In 1988 the World Meteorological Organization and the United Nations environment program established the Intergovernmental Panel on Climate Change (IPCC) whose job it is to produce reports evaluating the risk of climate change due to human activity. In 1992 the United Nations agreed on a Framework Convention on Climatic Change, which came into force in 1994. In 2006, ex-Vice President Al Gore's 2006 documentary "An Inconvenient Truth" highlighted the problem. In 1997 the Kyoto Protocol committed industrial countries to achieve quantified targets for decreasing the emission of greenhouse gases. Germany, for example, has already banned lignite. The United States agreed to reduce overall emissions of greenhouse gases to 5% below 1990 levels by 2008–2012 but has since withdrawn from this commitment. The Copenhagen conference of December 2009 was supposed to be a follow-up to the Kyoto Protocol of 1997 and to set legal limits for carbon dioxide emissions by the various world countries. It produced many declarations of benign intent but did not lead to a binding commitment or an extension of the Kyoto commitment period and was widely perceived to have failed. Further rounds of negotiations, for example, at Cancun, Mexico, in 2010 produced no breakthroughs.

There are various plans to tie up carbon dioxide in depleted oil reservoirs and unmineable coal beds⁷ or to sequester it in the ocean or to use it in enhanced oil recovery, and the idea of reducing one's "carbon footprint" is popular among people in developed countries who feel they want to make a contribution.

Whether or not the evidence on climate change is conclusive or merely likely, the things that combating global warming require us to do, such as conserving energy, are mostly good things, which we should be doing anyway, even if it later turns out to be for the wrong reason. Table 20.2 shows the world's ten largest greenhouse gas emitters.

As can be seen, rich countries are reluctant to restrain their profligate lifestyles. Poor countries feel that it is hypocritical that rich countries, who have brought about the problems, should now be asking them to abandon their short-term development plans in favor of relatively diffuse long-term objectives. Half of Africa's electricity, for example, is generated from South African coal, so that criticism of its contribution to pollution and global warming is muted. China is already exempt from the Kyoto provisions. Thus we must all hope that the predictions of the gloomiest proponents of climate change are wrong, because it is evident that only relatively few people are prepared to make the adjustments in lifestyle that would stabilize, let alone reduce, carbon dioxide concentrations in the atmosphere.

TABLE 20.2 Greenhouse Gas Emissions by Top Ten Emitters^a (2005)

Rating	Country	Global Emissions (%)	Metric Tons per Person per Year
1	China	17	5.8
2	United States	16	24.1
3	European Union-27	11	10.6
4	Indonesia	6	12.9
5	India	5	2.1
6	Russia	5	14.9
7	Brazil	4	10.0
8	Japan	3	10.6
9	Canada	2	23.2
10	Mexico	2	6.4
	All others	29	

^aThese values are for the GHG emissions from fossil fuel and cement production. Calculations are for carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), and gases containing fluorine (the F-gases HFCs, PFCs, and SF₆). The estimates are subject to large uncertainties regarding CO₂ emissions from deforestation; and the per country emissions of other GHGs (e.g., methane). There are also other large uncertainties which mean that small differences between countries are not significant. CO₂ emissions from the decay of remaining biomass after biomass burning/deforestation are not included.

Source: http://en.wikipedia.org/wiki/Kyoto_Protocol#cite_note-24. See also MNP (2007). "Greenhouse gas emissions of countries in 2005 and ranking of their per capita emissions." Netherlands Environment Agency website. [http://www.pbl.nl/images/Top20-CO2andGHG-countries-in2006-2005\(GB\)_tcm61-36276.xls](http://www.pbl.nl/images/Top20-CO2andGHG-countries-in2006-2005(GB)_tcm61-36276.xls).

20.2 RESOURCE DEPLETION

Predictions of resource depletion have a long history. In 1865 the British economist, W. S. Jevons (1835–1882) predicted the collapse of the British economy within a century because of the depletion of coal supplies.⁸ In 1898 Sir William Ramsey, discoverer of the inert gases, predicted world disaster by the middle of the twentieth century because of the depletion of "fixed" nitrogen. A U.S. Presidential Commission in 1922 declared "Already the output of natural gas has begun to wane. Production of oil cannot long maintain its present state." In 1977 U.S. President Jimmy Carter declared "We could use up all the proven reserves of oil in the entire world by the end of the next decade." The "Limits to Growth" forecasters of the 1970s saw the world running out of numerous nonrenewable natural resources within thirty years.²

None of these forecasts have been vindicated. Mercury reserves were supposed to be depleted within ten years, but consumption fell dramatically, as it was seen to be a dangerous pollutant anyway. Mercury cells for making chlorine and sodium hydroxide were replaced by membrane cells, mercury arc rectifiers were replaced by more effective solid state devices, amalgams ceased to be used for dental fillings, and even mercury in thermometers was replaced by alcohol or by thermoelectric materials. Compact fluorescent lamps that economize in electricity contain 1–5 mg of mercury and are a growing market, and there are campaigns to make sure they are disposed of

without the mercury being released into the environment. One of the few remaining uses for mercury is for the illegal extraction of gold from the Amazon basin, where it is discharged into the world's largest freshwater source, but the quantity of water in the Amazon is so huge that the mercury has not yet attained toxic levels and the process, while illegal, is not easy to police. It is alleged that coal-fired power stations emit some 2000 metric tons/year of mercury, and offshore oil and gas platforms may emit a similar amount, but the United Nations Environment Program just has not monitored it.⁹ Meanwhile, this is a pollution not a resource depletion problem, and forcing the offshore operators to trap mercury would both augment reserves and protect the environment.

Tin was another metal said to be facing rapid depletion. Instead, new can-making technology displaced its major use in food cans, and demand dropped to the point at which tin mines in southwest England, operated since the days of the Romans, have had to be decommissioned.

Reserves-to-production ratios of other nonrenewables have, if anything, increased over the past thirty years. Hydrometallurgical techniques, for example, have made accessible large deposits of copper in spoil heaps around the world, left over by less efficient methods of extraction. Exploration has discovered fresh reserves. The industrialists' claim that "If you have thirty years reserves under your belt, you don't bother to look for more" seems to have at least an element of truth about it.

There is concern at the time of writing about rare earth metals (lanthanides). The Chinese produce about 97% of world supplies and have decided to cut their export quotas by 11%. Neodymium is of importance in wind turbines; other rare earths are used in mobile phones and flat-screen televisions. Rare earths fortunately are not, in fact, rare. Mines that were closed in Australia and the United States because they could not compete with Chinese prices are now reopening. There may be a glitch in supply, and it may be necessary to exploit more dilute ores, but resource depletion does not come into it.

This optimistic conclusion applies only to mineral resources. Energy is plentiful if shale gas is accessible; it is the carbon dioxide that is the problem. Problems of food shortages and population pressures will be discussed in the next section.

20.2.1 Food, Water, and People

20.2.1.1 Food

Can the earth feed 9 billion people? The answer, surprisingly, is "yes." World cereal production is approximately 2000 million metric tons (in 2007: wheat 607 million metric tons, maize 784, and rice 651). Taking these three products alone, the world produces 2000 million metric tons = 2×10^9 metric tons = 2×10^{12} kg. One kilogram of wheat, after milling, provides about 3000 (big) calories. So these three products provide 6×10^{15} big calories.

A population of 9 billion can live on 2000 big calories each per day. Thus the annual world requirement for 9 billion (and world population is still short of that) is $9 \times 10^9 \times 2000 \times 365 = 6.57 \times 10^{15}$ big calories.

The world already produces enough cereals alone (ignoring meat and fish, fats, and oils) to feed 9 billion people. The catch, of course, is that much of the cereal produced goes to feed cattle to provide meat for the more prosperous members of the population. But the calculation illustrates the point that there is already enough food to go around; the problem is one of distribution. It also one of conflict. There are few famines even in desert lands where there is not some sort of war in progress.

Not only that, the productivity of agriculture in developing countries is low. We offer a single example of dysfunctional government in Africa, told to us by a senior civil servant. Farmers in many countries are obliged to sell surplus grain to a corrupt state-run marketing board, which pays them a pittance and then redistributes the grain to the army, to keep them loyal. Owners of smallholdings are discouraged from investing in fertilizers, machinery, and high-yielding plant types, because they get paid too little. They have no way of offering their grain, fruit, or vegetables on a free market. Thus they grow enough for their own family's needs. Hong Kong was a prime example of a country with scarcely any arable land, which was still self-sufficient for food because the farmers were able to bring their produce to market and sell it at the economic rate. With relatively honest government and access by farmers to free markets, developing countries' agricultural production could soar. The addition of genetically modified crops, opposed by Europe, could improve food outputs even further.

20.2.1.2 Water

The next problem is water – essential for successful agriculture. The amount of water on earth is constant and huge, but little of it is accessible for human use. Ninety-seven percent is salt water primarily in the oceans. Of the remaining 3% that is fresh water, two-thirds is frozen in glaciers and the polar ice cap. Most of the remainder is groundwater, existing in aquifers – some of them accessible – below the earth's surface. That leaves a small fraction – about 0.3% of fresh water – as surface water. Eighty-seven percent is in lakes, 11% in swamps, and 2% in rivers.¹⁰

Of the available fresh water, 69% is used for irrigation, 22% by industry and 8% by households. Domestic uses are therefore a relatively small burden on water supplies. Meanwhile, U.S. citizens used about 570 liters/day/person in 2006. The French used 290 liters, the British 150 liters, the Indians 130 liters, and the Ugandans about 15 liters.¹¹ These domestic uses, however, require high purity water. Contamination by bacteria from sewage is the source of waterborne diseases such as cholera. The problem is particularly acute in refugee camps, where fecal material dumped in a river upstream infects others who draw water from the river downstream. Provision of clean water has nonetheless been one of the successes of governments and aid agencies. The proportion of people in developing countries with access to safe water is calculated to have improved from 30% in 1970 to 71% in 1990, 79% in 2000, and 84% in 2004.

Demands on water supplies are increasing and politicians are fond of saying that the next batch of wars will be about water not oil.¹² The developed nations will probably have adequate water supplies at least until 2025, but elsewhere, because of

population growth and rising living standards, many of the world's major aquifers are becoming depleted. Irrigation in dry areas such as northern China and India is supplied by groundwater, and it is being extracted at an unsustainable rate. Mexico City, Bangkok, Manila, Beijing, Madras, and Shanghai have all experienced drops in aquifer levels of between 10 and 50 meters. Excessive pumping can lead to the leaking of salt water into the aquifer, rendering it undrinkable.

Water pollution can be avoided by the construction of adequate sewage treatment systems and chlorination facilities (Section 20.4.4). There is huge scope for water management systems. Even desert areas usually have two or three torrential rainstorms per year, and systems of dams can retain much of the water. The Nabateans managed it 2000 years ago, so it should not be impossible now.

Irrigation methods such as furrow and overhead sprinkler irrigation are inexpensive, but much of the water evaporates, runs off, or drains rapidly below the plant root. Drip or trickle irrigation has higher capital costs but is more efficient. This is an area where Israel is a world leader, but political factors inhibit export of its expertise.

Water supplies can also be augmented by desalination (Section 9.1.2.3) but, even though the cost of desalinated water has dropped, it is still expensive to use for agriculture even though it is fine for tourism. The cost of providing desalinated water for a U.S. tourist (570 liters at 50¢ per metric ton) is about 28.5¢ per day. Oranges require 149–490 liters/kg,¹³ therefore 7.5–24.5 ¢/kg or 2–6 ¢ per typical 250 g orange, without any other costs being taken into account. Thus desalination is economic for domestic use and for high value agricultural produce, but crops should be grown either where water management or natural rainfall provides adequate supplies of water. It used to be said that Kansas could grow enough grain to feed the whole of the United States, and that the grain belt could feed the whole world. Israel imports grain from the United States because it is still cheaper than desalinating water to grow its own grain. But the use of grain to make biofuels, and the enthusiasm for renewable (i.e., agricultural) feedstocks for the chemical industry means that there is going to be a competition for land between food and feedstocks. That is why so much work is in progress on processes that use switch grass and other plant materials that do not require land or water supplies of agricultural quality. It also raises problems with the clearance of forest to provide more cash crops.

An unknown quantity is the effect of shale gas mining. This consumes large volumes of almost pure water, which is pumped into shale layers about a kilometer below the surface. How much will this increase the demand for fresh water, and what happens in the long term to the water pumped underground?

20.2.1.3 People

The prehistoric population explosion came with the victory of Neolithic over Paleolithic man between 8000 and 5000 B.C. Herdsmen-farmers supplanted hunter-gatherers because farming could support far larger populations. Although the transition took over 3000 years, it was still a significant shift. By the time of Malthus, the population was beginning to overwhelm natural resources. Centuries of poor farming practice turned much of the fertile Mediterranean basin to desert.

Goat farming was partly responsible as was the habit in the Ottoman Empire of chopping down trees as a punishment for nonpayment of taxes or animosity to the Caliph or because the soldiers didn't have anything else to do.

Between 1798 and 1826 Thomas Malthus propounded his famous theory that the power of population is indefinitely greater than the power in the earth to produce subsistence for humans. Populations would live perpetually at subsistence level because any surge of food supply would be met by an increase in population. Always population would be limited by disasters, war, famine, and disease. Population increased exponentially, while food supply increased linearly. Malthus was unfortunate in his timing because he wrote just as the Industrial Revolution was happening. Farming-herding was being overtaken by factories. The augmentation of muscle power by steam and later gasoline power gave humankind vast new resources. The world population expanded at an ever-increasing rate. This is not must journalese. Between 1650 and 1700, world population rose from 500 to 575 million, and there was annual excess of births over deaths of 2.8 per 1000. Between 1950 and 2000, it rose from 2500 to 6250, with an annual excess of 18.5 per 1000.

The rapid increase had two causes. One was the increase in global prosperity with a concomitant increase in food supply brought about by mechanized farming, pesticides, improved grain species, and so on. The other was the realization that fairly simple public health measures (clean water, immunization, and so on) could reduce death rates from disease.

But the increase was no longer rapid between 1950 and 2000 in developed countries. In the United States, Russia, and Europe birth rates had dropped as fast as death rates. Educated populations (necessary to operate the factories) realized that fewer children could be brought up under better conditions; families could enjoy themselves at a standard of living far above subsistence. Increasingly sophisticated contraceptive methods separated sex from procreation. Television provided something else to do in the evenings, and greater equality for women meant that they were more interested in careers and less in endless pregnancies. By the end of the millennium, the average woman in developed countries was not producing even enough children to maintain the population.

The world's highest crude birth rates are in developing (or perhaps *not* developing) countries. Niger, Mali, Uganda, Afghanistan, and Somalia had birth rates between 51.6 and 43.7 per thousand persons between 2005 and 2010. The world average was 19.95. The highest developed country birth rate was New Zealand (134.94) ranked 137 in the world, with the United States just behind at 13.82. The European Union 27 had an average of 9.9, with the United Kingdom 10.65. Spain and Italy, two Roman Catholic countries, where one might expect high birth rates, have rates of only 9.72 and 8.18, and the Japanese have a rate of only 7.64, practically the world's lowest.¹⁴ In the words of Gus Kahn and Raymond Egan's 1921 hit, "There's nothing surer, the rich get rich and the poor get children."

Countries with very high birth rates have one set of problems; those with low birth rates another. If one's population is growing at 3% per year, as is the case in the most fertile countries, the economy has to expand at the same rate just for things to stay at the same level. Perhaps half the population will be under twenty with little hope of

employment. In agricultural economies, farmers will be pushed higher and higher up hillsides to try to farm less hospitable land.

Low birth rate developed countries have the opposite problems. Their populations are ageing, and there are fewer economically active people to support them. To do the unattractive jobs, immigrants are invited in, who, in many cases, bring with them cultural baggage that may not fit in with the traditions of the host country. The British attracted immigration from the Indian subcontinent and the West Indies, the Germans imported Turks, and the French brought in Algerians. The United States, a country of immigrants, imported Hispanics. In principle, the immigrants should plug the gap left by the low indigenous birth rates, but it does not seem to work like that. Many of the newcomers find themselves in ghettos and there are problems with school and with languages.

Some of the difficulties are exemplified by China. The Chinese government, hamstrung by its high birth rate, took punitive measures against town dwellers who had more than one child and country dwellers who had more than two. This brought down the birth rate to 14 per 1000 and contributed to their recent economic success. But they are now faced with the serious problems of an ageing population and are wondering whether to relax their population control measures.

20.3 ENERGY SOURCES

The area of ongoing concern, however, is that of energy.¹⁵ The world as a whole, and the chemical industry in particular, relies on supplies of fossil fuels to support its lifestyle. In 2008, the world consumed 11,295 million metric tons oil equivalent (MTOE). The United States was the most profligate consumer. With 4.5% of the world population, it consumed 2299 MTOE – 20.4% of the total. The Chinese with 19.6% of world population, consumed 17.7%, a figure that has doubled since 2001 and quadrupled since 1984. The Indians, with 17.3% of world population, only consumed 3.8% of world energy. Thus Americans annually consume 7.4 metric tons of oil equivalent per capita, more than twice as much as Europeans and twelve times as much as the Indians, who consume 0.37% (Table 20.3).

The pattern of primary energy sources varies from region to region. In Southeast Asia, coal accounts for about 48%, whereas in the United States, it is about 25%, and in Europe, where the coal is more deeply buried and difficult to mine, about 18%. China (66%) and India (49%) get most of their energy from coal. Hydroelectricity provides 6.3% of world energy and 2.5% of U.S. energy and is generally small except in countries well endowed with mountains and water. In Norway it accounts for 69% of the total primary energy consumption, and in Central and South America, Canada, Switzerland, and Austria it accounts for about a quarter of consumption. Nuclear energy has 11% of the energy supply in the European Union and 8.3% in the United States but little elsewhere.

Where are these huge quantities of energy to come from in the future? Sixty percent of long term oil reserves are in the Middle East, another 6.4% in Libya and Nigeria, and 9.5% in the Russian Federation and Kazakhstan. North America including

TABLE 20.3 World Population and Energy Consumption^a (2008)

Country	Energy Consumption (MTOE)	Population (millions)	Percentage (%) World Energy	Percentage (%) World Population	Tons per Person
United States	2299	308.6	20.4	4.5	7.4
European Union	1728.2	501.3	15.3	7.4	3.4
Japan	507.5	127.5	4.5	1.9	4.0
CIS	684.6	142	6.1	2.1	4.8
China	2002.5	1336	17.7	19.6	1.5
India	433.3	1177	3.8	17.3	0.4
World	11294.9	6801.4	100.0	100.0	1.7

^a If everyone used as much energy per person as in the United States, 50,330 MTOE would be required, that is, 4.5 times as much as at present. Nine billion people at the same level would require 66,600 MTOE, that is, 5.9 times as much.

Source: BP Statistical Review of World Energy.

Mexico still has 5.6% of reserves and Venezuela 7.9%, but that is a long way from Pan-American self-sufficiency. The European Community has a miserly 0.5%, which reflects itself in many ways including foreign policy. Gas reserves are slightly less biased to the Middle East, which has only 41%. The Russian Federation has 23.4% and North America 4.8%, although this last figure will be revised sharply upwards if shale gas turns out to be environmentally acceptable, as it probably will.

How fast will these reserves be depleted? Coal will last for over 100 years even with the recent rise in consumption. But it is dangerous to mine and polluting to burn. The U.S. government in 2010 was still regarding it as a worthwhile energy reserve. Nuclear energy is boundless but carries its own unique dangers; and, if nuclear power is adopted worldwide, there are going to be problems with high grade uranium ores. Hydroelectricity is renewable but not available on the scale that the world requires. And oil and natural gas? Here is the difficulty. In spite of their lavish exploitation, reserves are larger than they were 30 years ago, when Meadows et al.² predicted their rapid depletion. The reserves-to-production ratio dropped from about 35 to 28 years in the 1970s, hence the prophecies of doom, but rose to a peak of 43 years in 1992, partly because of a reassessment of Saudi reserves. It has since dropped back to 42 years. Natural gas coasted along at 50 years in the 1970s, rose to 58 years for most of the 1980s as a result of discoveries in the Soviet Union, peaked at 67 years in 1992, and has since dropped back to 60 years.

Everyone is agreed that fossil fuel reserves are finite, but there is no way of knowing how finite. Current “wisdom” expects “peak oil” in 2015. It is getting more difficult every year to locate additional reserves, but the world is getting better at it. The reserves would last dramatically longer if energy conservation were a priority. Non-Americans are baffled as to why U.S. and Canadian citizens need to use twice as much fuel as anyone else, even people in other developed countries. Conservation would also decrease carbon dioxide pollution and impact on global warming, but the question of how finite is finite would still exist. Unconventional methods of generating energy have made slow progress.

Before discussion of these options, however, mention should be made of enhanced oil recovery. A time may come in the life of an oilfield when the natural pressure of the reservoir has dropped to the point at which it is no longer sufficient to force the oil out of the pores of the rock into the bottom of the well. At this point, as much as 80% of the oil may remain in the ground. It can be displaced by enhanced oil recovery – the injection of fluids – to force out the remaining oil. Water is widely used, sometimes mixed with a water-soluble polymer to increase its viscosity or reduce its mobility. Steam may be used to reduce the viscosity of heavy crudes. Hydrocarbon gases may be injected or even carbon dioxide, this last also being a way of reducing carbon dioxide in the atmosphere. It is unclear how much oil remains in oil wells. Enhanced recovery in 2000 was approximately 3% of total oil production. In the mid-1970s, BP was talking about having raised typical extraction rates to 40%. One estimate from the early 1990s was that global petroleum reserves were about four times proved reserves but not all this petroleum can be recovered economically. Indeed, the very fact of its remaining in place indicates the expense of bringing it to the surface.

20.3.1 Wind Power

Wind power is a renewable source of energy on which substantial research has been done. Global total wind capacity by 2009 was 158 GW, about 1.13% of world energy consumption, and about a sixth of hydroelectricity's 6.35%. Germany (25.8 GW), Spain (19.1 GW), the United States (35.2 GW), and China (25.1 GW) are the largest wind power nations. The United Kingdom is the windiest country in Europe, and this means that a British turbine produces on average 65% more electricity than one in Germany. The United Kingdom still lags behind with only 4 GW, and it is widely believed that much of the wind is generated by political speeches in favor of wind power, rather than the harnessing of the natural resource. Wind energy, unfortunately, is intermittent and unpredictable. In Britain, turbines operate at about 28% capacity and in Germany about 21%, compared with coal-fired power stations at about 75%. The best locations for wind farms are in remote areas, but this leads to losses when the electricity is transferred to users. Typical offshore turbines are 70 m tall with three 50 m blades generating 3–5 MW but future ones may be larger whereas onshore installations will be smaller, generating about 2 MW. They make a visual impact on remote areas and are therefore a target for some groups of environmentalists. Planning permission in developed countries is frequently withheld. The future of wind power may rest with offshore turbines, which are feasible but cost 30–50% more. It is hard to see wind power ever contributing more than a few percent of energy demand, although the UK government is targeting 10% and the Danish government 40%.

Wind turbines depend on neodymium, a metal on which the Chinese have a virtual monopoly (Section 20.3). They are threatening export restrictions. Neodymium is mined and processed under conditions that would not be tolerated in the developed world, and if more dilute ores have to be mined under better conditions, the cost would be substantially higher, which might affect the economics of the turbines.

20.3.2 Wave Power

When the second edition of this book appeared, only one fully operational wave-energy power plant existed, based on the Isle of Islay in northwest Scotland. The design was based on an oscillating wave column and a so-called Wells turbine. The oscillating wave column consisted of a container, broad at the bottom with a hole in it, which sat 2.5 m below sea level, together with a narrow top above water level leading to the turbine. As the wave passed, water streamed through the hole and compressed or rarefied the air above it. The Wells turbine has the unique property of turning in the same direction regardless of which way air flows over the turbine blades, hence it is driven systematically by the rise and fall of the water level.

Since then, numerous technologies are being planned, including experimental rigs, and many operating on a small scale. The Aguçadoura wave farm was the world's first wave farm and was located 3 miles off the coast of Portugal, near Oporto. The farm was designed to use three Pelamis wave energy converters, consisting of three floating tubular generators, each about 160 m long. The hinged sections of the device move with the waves, and the motion between one section and the next creates pressurized oil to drive a hydraulic ram that drives a hydraulic motor, which in turn generates electricity. The farm first produced electricity in July 2008. It was opened officially on 23 September 2008 and was shut down after two months because of the financial collapse of the operators. Another Pelamis wave farm is under construction 1.2 miles off Billie Croo near Stromness, Scotland,¹⁶ which will have four generators (3000 kW), one of which is already on stream. The Pelamis system is in competition with the "Oyster Calm" system of Aquamarine. Then there are underwater systems such as the Norwegian "Hammerfest Strom" and the "Marine Current Turbines" as well as a new "doughnut" device.¹⁷ Nineteen systems are listed by Wikipedia.¹⁸

The use of tidal power rather than waves is another possibility. Wave power derives from the regular rise and fall of waves, whereas tidal power relies on the longer term flows of seawater powered by tides and ultimately by the moon. Turbines can be installed in tidal races such as the bottleneck between an island and the mainland, and operate like underwater windmills. Alternatively, a tidal barrage could operate like a hydroelectric scheme, but the smaller drop for the water means a much longer dam for a given capacity. Also, the tides are only useable for about ten hours per day. A single European plant operates at Rance, near St. Malo, where the difference between the ebb and flow tides is a remarkable 15 m (50 ft). Readers of Dumas' *The Count of Monte Cristo* will recollect that the tide comes in with the speed of a galloping horse.

The Scottish government has approved plans for a 10 MW array of tidal stream generators near Islay, Scotland, costing £40 million and consisting of 10 turbines – enough to power over 5000 homes. The first turbine is expected to be in operation by 2013.

Meanwhile, the setting up of a wave or tidal power plant is expensive, and power from the sea is a long way from widespread application. Will the energy required to build the devices even be matched by the energy produced during their lifetimes? Early estimates are that present technology can produce electricity at about 20¢ per kWh, far more than a fossil-fuel power station.

20.3.3 Solar Power

In a sunny climate, solar energy provides about 800 watts per square meter. This is the intensity of radiation received if one sits 10 cm from a 100 watt incandescent electric light bulb. Solar energy equivalent to the total world fossil fuel energy reserves falls on the earth in less than 14 days, and the annual world's energy requirement within 26 minutes. The problem is to concentrate the energy.

In 2008, roof-mounted water heaters, deriving energy from the sun, accounted globally for 120,000 megawatts of capacity, enough for 27 million homes. China has two-thirds of the capacity, but its population is of course very large. On a per capita basis, Cyprus and Israel are the leading nations with 0.9 and 0.7 m² per person. This is about 3.5% of energy requirements in Israel. Simple pumping and reflector systems provide hot water in sunny climates pretty much all the year round, although an electrical heater is usually added to provide backup.

Various methods are used to convert solar energy to electricity: concentrated solar power (CSP) and photovoltaic cells.

20.3.3.1 Concentrated Solar Power

In concentrated solar power (CSP) installations, parabolic mirrors concentrate sunlight onto pipes containing a high boiling liquid, and the heat is then used to raise steam, which operates a Rankine cycle engine to generate electricity. This is the conventional steam operated heat engine, found in most conventional power plants but with a higher boiling working fluid than water. The mirrors automatically track the sun during the day. Interest recommenced in 2006 onwards after a 16 year hiatus. World capacity has grown since then to 820 MW, and projects in the pipeline should quadruple this. The technology is operated on the largest scale in the Mojave Desert in sunny California, where there are nine SEGS (solar energy generating systems) plants. The capacity is 354 MW thermal power installed capacity, making it the largest installation of solar plants of any kind in the world. The average gross output is around 75 MW of electrical power – an efficiency of 21%. In addition, the turbines can be used at night by burning natural gas.

A smaller installation exists in Sicily near Syracuse, where Archimedes, who gave his name to the project, originated. Output was supposed to reach 5 MW by 2009 and 200 MW by 2012. CSP installations have low running but high capital costs. The chief maintenance required is repair of wind damage to the mirrors.

Solar ponds, pioneered in Israel, produce a temperature difference of 60–70°C, which can be used to drive generators, but are hampered by high capital cost and low thermodynamic efficiency.

20.3.3.2 Photovoltaic Cells

Generation of electricity from solar energy via photovoltaic cells has been doubling every two years, increasing by an average of 48% each year since 2002, making it the world's fastest-growing energy technology. At the end of 2008, the world capacity reached 15,200 MW. About 8000 MW was installed in 2009 and double that in 2010.

Many solar panels are in small-scale applications such as parking meters, but experimental solar power stations have capacities ranging from 10 to 60 MW. Scaling up to 150 MW is planned. Annual production reached nearly 7000 MW in 2008, much of this being produced in China and exported. There is activity also in Japan and Germany.

The leader in this field in terms of installed capacity, surprisingly, is Germany. In spite of its low levels of sunshine, it boasts 5308 MW. Spain comes second with 3223 MW, and Japan and the United States third and fourth with 2149 and 1173 MW, respectively.¹⁹

Israel is active in solar energy. Ketura Sun, built on Kibbutz Ketura in the Negev, is its first commercial solar field. It came on stream in 2011, covers 20 acres, has 18,500 photovoltaic panels, and is expected to produce green energy amounting to 4.95 megawatts.

A first generation photovoltaic cell consists of layers of crystalline silicon alternately doped with boron and phosphorus to make them *n*-type and *p*-type semiconductors. When light falls on the cell, the atoms in the *p*-type layer become excited and emit an electron, which passes to the *n*-layer. Excess electrons in the *n*-layer pass to the *p*-layer and the holes in the *p*-layer transfer to the *n*-layer. This creates surpluses of electrons and holes at the semiconductor junctions. A metallic grid on top of the photovoltaic cell collects the electrons and transfers them to the electron deficient junction via an electrical circuit. An array of photovoltaic cells is covered with glass to protect it from the weather and the glass has an antireflective coating to prevent light from being reflected away from the cells. Such photovoltaic cells produce electricity at efficiencies between 10% and 20%, but widespread use is inhibited by the high cost of the very pure silicon, gallium arsenide, or gallium antimonide required.

Second generation cells, known as “thin cells,” use films of semiconductors such as cadmium telluride and copper indium selenide rather than sliced wafers of silicon, making them less expensive to manufacture. They are cheaper than silicon cells but not as durable and efficient.

A subset of photovoltaics is concentrated photovoltaics (CPVs). The response of a photovoltaic cell is approximately linear with light intensity. Thus a way of saving on expensive silicon is to have a mirror instead that focuses sunlight onto a photovoltaic cell. Solar concentrators of many varieties are used. The drawback is that even the best cells are only 40% efficient, and the remainder of the incident radiation is degraded as heat. Cooling is essential and this adds to the cost.

A novel thermochemical reactor has been developed at ETH, Zurich. Concentrated solar radiation enters a reactor, is intensified by a parabolic mirror system, and is focused on a cerium oxide cylinder. Water and carbon dioxide are fed into side inlets and oxygen, hydrogen, and carbon monoxide emerge at a bottom outlet. Impressive though this is in chemical terms, the solar energy conversion efficiency of about²⁰ 0.8% suggests that this, like so many other ingenious schemes, has little chance of commercialization.

20.3.3.3 Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSSCs) were first developed in 1991.^{21,22} The cell consists of two sheets of conducting glass. One plate of glass (the working electrode)

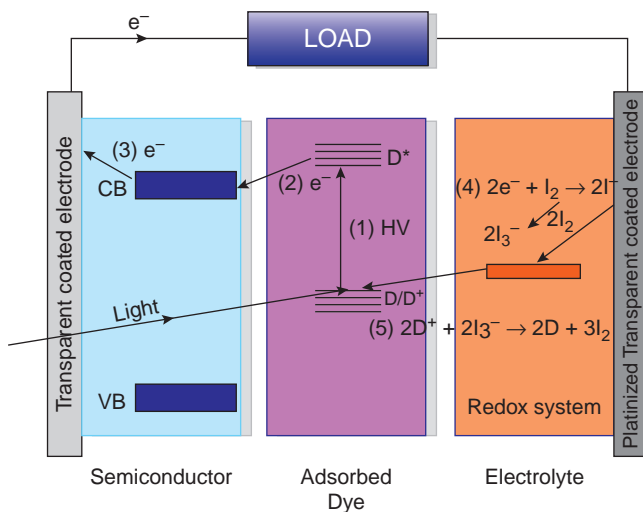
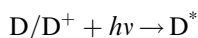


FIGURE 20.1 Dye-sensitized solar cell: energy levels representation. (Height on diagram corresponds qualitatively to energy level.)

is coated with titanium dioxide nanoparticles that have an organometallic amphiphilic ruthenium sensitizer dye adsorbed onto the surface. The other (the counterelectrode) is coated with a catalyst (platinum or carbon). The cell is filled with an electrolyte solution containing a redox couple (usually I_2/I_3^-) to regenerate the dye. Figure 20.1 illustrates the principle, although the adsorbed layer and the semiconductor layer are not separate in practice but intimately mixed.

The cycle is as follows:

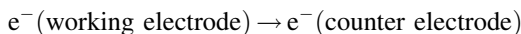
1. The dye absorbs sunlight and passes to an excited state:



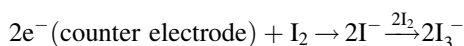
2. The excited state interacts with the conduction band (CB) of the semiconductor, leading to electron transfer:



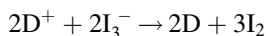
3. The electron passes through the circuit from the working electrode to the counter electrode, giving an electric current:



4. The electron at the counter electrode reduces the electrolyte:



5. Finally, the dye is regenerated:



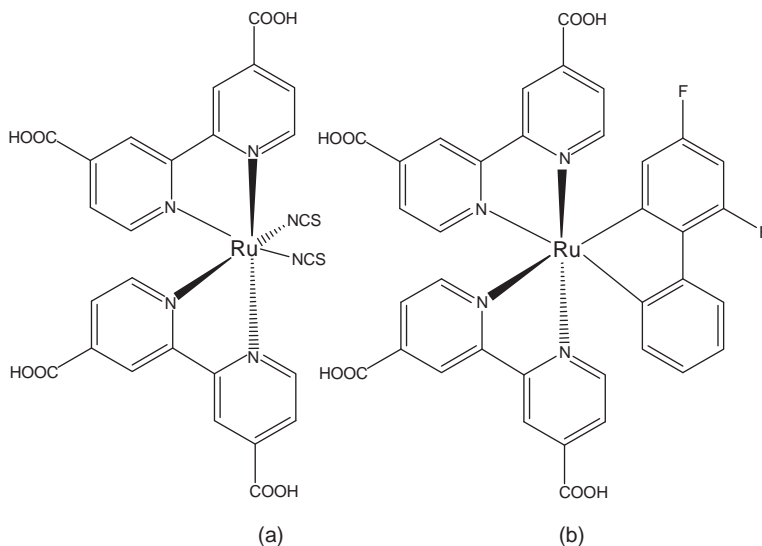


FIGURE 20.2 Ruthenium dyes for dye-sensitized solar cells.

The original dye (Fig. 20.2a) was one of the most efficient, but the presence of thiocyanate groups limited its chemical stability and hence the lifetime of the DSSC. A more recent modification replaces the thiocyanate groups by a ligand that forms two bonds with the ruthenium(II). The two fluorine atoms fine tune the redox potential of the complex, ensuring that it does not become too strong an electron donor. In order to regenerate, the dye must be able to regain the electron it loses when exposed to light. Various other dyes have been tried, and the field repeatedly reviewed.²³ Cobalt sulfide has recently been suggested as a replacement for the expensive platinum cathode.²⁴

Photovoltaic cells are 12–18% efficient, although one company claims 23%. At present, the ruthenium thiocyanate cell is only 11% efficient, and the new cell is worse than that. On the other hand, it is cheaper to make and involves fewer toxic materials in its production. A general drawback of solar cells is that they produce direct current. For charging mobile phones or laptop computers, this is excellent, but if they are to integrate with the grid, their output must be converted to alternating current. Meanwhile, this is seen as an exciting emerging technology and the first commercial shipment of DSSC solar modules occurred in July 2009. Dyesol/Tata steel appears to be the market leader.

20.3.3.4 Artificial Photosynthesis

Nature uses solar energy to convert carbon dioxide and water to carbohydrates by means of the catalyst chlorophyll. Sugar cane is said to be the most efficient photosynthesizer but only achieves an efficiency of about 1%. A research aim is the development of a photosynthetic catalyst with a higher efficiency than chlorophyll, and it is being encouraged by the National Science Foundation, which has

established a center to develop artificial photosynthesis²⁵ systems. The feedstock would have to be carbon dioxide or water or both. Water requires only 238 kJ/mol to split it into hydrogen and oxygen; carbon dioxide requires 283 kJ/mol to give carbon monoxide and oxygen. Carbon dioxide and water will give methanol at a cost of 703 kJ/mol. These energies correspond to wavelengths of light of 502, 422, and 170 nm, respectively. The first falls acceptably in the green region of the spectrum, the second is in the blue, but a high proportion of visible light will be useless, and the third is in the vacuum ultraviolet and could not be brought about by solar energy in a single step. Much research has focused on mimicking chlorophyll and trying to produce multistep reaction carbon dioxide absorbing systems, many of which are based on porphyrins, but no breakthroughs are in sight. Thus the work that seems to offer the best prospects – and even these are long in the future – has concentrated on splitting of water.

Catalysts that can generate hydrogen from water are well known. The problem is that they contain expensive metals such as platinum and often work only with ultraviolet light rather than sunlight. A German team has reported that a polymeric form of carbon nitride light-emitting diode will generate hydrogen from water when exposed to sunlight. Unfortunately, it operates very slowly, although this can be increased by creating a highly porous version of polymer. It could also be speeded up by doping with platinum, although this removes the cost advantage over platinum-based systems. Similarly, the Japanese report that they can generate hydrogen from water via the catalyst $(\text{Ga}_x\text{Zn}_{1-x})(\text{N}_x\text{O}_{1-x})$. The real crunch, and this applies to all photosynthetic systems, is what to do with the leftover oxygen atoms. They have a tendency to recombine with the hydrogen atoms, wrecking the whole process. Finding a way of coping with the oxygen is the key to any artificial photosynthesis process. Systems based on ruthenium show some promise. Other ideas abound. An Australian group has synthesized a structure in which four manganese and four oxygen atoms are bound together in a cube shape, and they calculate that this structure, incorporated into a *Nafion* polymer, should be able to oxidize water.²⁶ They have also used the conducting polymer PEDOT (Fig. 17.14) coated on a porous Goretex membrane to replace platinum electrodes.²⁷ It can match the oxygen reducing ability of platinum and, unlike platinum electrodes, it is not poisoned by carbon monoxide, a possible contaminant in fuel cells (see below). An Israeli group has developed a novel molecular construct based on ruthenium that generates hydrogen from water via a heat treatment process, and then generates oxygen via a light-driven process. A group at Penn State has developed an array containing two different types of titanium dioxide nanotubes and shown that it can split water, when exposed to sunlight, with hydrogen produced by one of the nanotubes and oxygen by the other, but the conversion efficiency is only about 0.3%.

Dan Nocera of MIT said in an interview in 2007 that “There are two keys – one is you have to make photovoltaics cheaply, so you can mass-manufacture rather than have to make them a panel at a time. The second thing to figure out is the reaction chemistry on how to split water to hydrogen and oxygen. We don’t know how to do that yet, even though plants do it every day. We can do the hydrogen part pretty well, but we still have no idea how to get the oxygen out – and you want to do that because

you want a closed thermodynamic cycle.”²⁸ He has since announced an “artificial leaf” based on cheap materials (nickel, cobalt, and phosphorus) that works at an environmentally attractive neutral pH to release oxygen from water. The mechanism of catalysis is not clear. A current is run through an indium tin oxide (ITO) anode placed in a solution of cobalt and phosphate salts. Co^{2+} ions lose electrons to the anode to form Co^{3+} , which joins with phosphate ions to form a thin film on the anode. After possible further oxidation to Co^{4+} ions, the catalytic film abstracts electrons from water, leaving oxygen atoms and protons behind. At the surface of the film, oxygen atoms are brought together, and oxygen gas bubbles from the anode. Cobalt collects electrons and goes into solution as Co^{2+} species – ready to be regenerated by oxidation and returned to the catalyst. Meanwhile, the protons in solution are carried by phosphate anions to a conventional platinum cathode where they gain electrons to form hydrogen.²⁹

Nocera’s “artificial leaf” is about 10 times more efficient at carrying out photosynthesis than a natural leaf. It is compact and, placed in a single gallon of water in bright sunlight, the device could produce enough electricity (by processing the hydrogen in a fuel cell) to supply a house in a developing country with electricity for a day. Meanwhile, families in developing countries get ample sun and don’t use much electricity. The human ingenuity invested in artificial photosynthesis is much to be admired, but the process is still a long way from commercialization.

20.3.4 Nuclear Energy

Nuclear energy is a well-established technology, which many see as the solution to the energy and the global warming problems. In 2011, nuclear power stations produced 6% of world energy and 13–14% of world electricity, mainly in the United States, France, and Japan. On the one hand, nuclear power stations do not produce carbon dioxide. On the other hand, they are liable to accidents, such as Japan’s Fukushima disaster in 2011, which release radioactive material over a wide area. In addition, there is the problem of disposing of radioactive waste when a reactor reaches the end of its life. The waste is said to have a half-life of 25,000 years, about three times the period since Neolithic humans started farming and herding.

The nuclear industry has had a fairly good safety record since the explosion of the poorly designed Chernobyl reactor in 1986. That was until the Fukushima disaster in 2011. As a result, Germany has decided to phase out all its reactors by 2022 and Italy has banned nuclear power for a long time. Everyone is going to think long and hard before installing nuclear power, although countries not in earthquake zones need not really fear a Japanese-style disaster.

One problem facing builders of nuclear power stations is depletion of high quality uranium ore. Uranium is fairly abundant but in very low concentrations. Economically recoverable reserves are still estimated at over a hundred years, but if there were a large increase in the number of reactors, poor quality reserves would have to be exploited. Hydrometallurgical techniques make this a possibility. The main cost of nuclear power, however, is the building of the power station, so depletion of reserves is not a serious danger.

If uranium supplies were depleted, furthermore, there is the option of building breeder reactors, which produce more fuel than they burn. These have been built in several countries and the technology seems to be understood.

Fusion reactors that use the same nuclear reaction as the sun have been investigated for half a century but commercialization still seems in the realm of science fiction.

While there is a danger of reactors being destroyed in earthquakes or simply malfunctioning, the main worry associated with nuclear power is the proliferation of nuclear weapons. North Korea and Pakistan already have weapons; Iran is about to acquire them. There is a terrifying prospect of countries with ideology-driven or power-mad leaders having nuclear reactors on which weapons could be based. Sooner or later, one or several of them is likely to go off.

Discussion of nuclear technology is beyond the scope of this book, but we suggest that, while nuclear reactors outside earthquake zones are an excellent means of generating energy without carbon dioxide emissions, there are long-term risks associated with long-lived nuclear wastes, accidents, and nuclear proliferation.

20.3.5 Methane Hydrate

Because of water's hydrogen bonding, ice has an open structure and there is space within it for methane molecules to be trapped.³⁰ The combination, which is not chemically bonded, is a clathrate and is known as methane hydrate. Figure 20.3 shows the structure. Although it looks like ice, it is a poor conductor of heat and feels like expanded polystyrene. When ignited, it burns, leaving a water residue.

Until the 1970s, methane hydrate was merely a nuisance that plugged natural gas transmission lines when the weather was cold. In the 1960s, it was realized that

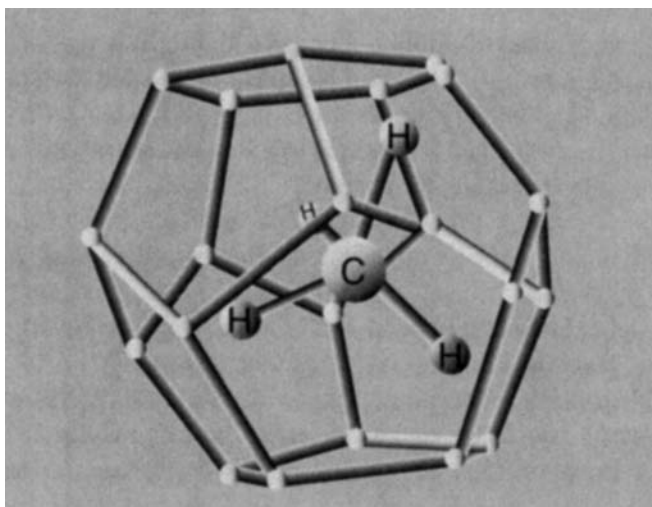


FIGURE 20.3 Methane hydrate structure showing carbon (center) and hydrogen (attached to the center) trapped in an ice lattice. (*Source*: USGS.)

it occurred naturally and, since then, it has been found to be ubiquitous. The United States Geological Survey now estimates that methane hydrate may contain more organic carbon – perhaps twice as much – as all the world’s reserves of coal, oil, and nonhydrate natural gas combined. The reservoir is in constant flux, absorbing and releasing methane in response to ongoing natural changes in the environment. The United States Methane Hydrate Research and Development Act of 2000 launched a program to investigate this unsuspected source of methane locked up in polar permafrost and the deep oceans (because the hydrate is stable above 0°C at high pressures).

The downside is first that there is no obvious way to mine the methane inexpensively, and second that methane is a greenhouse gas, 62 times as potent as carbon dioxide. Global warming of the permafrost as a result of current carbon dioxide emissions could melt some of the permafrost and release quantities of methane from the hydrate that could precipitate runaway global warming. The implications of this vast, dynamic, and previously unnoticed methane reservoir on long-term climate stability, sea floor stability, and long-term fuel reserves are only just being recognized.

20.3.6 The Hydrogen Economy

The media are full of predictions that the energy source in the future world will be hydrogen. Hydrogen, it is said, is nonpolluting and it combusts to give nonpolluting water. The source material (water again) is ubiquitous. There are several obvious objections to the proposal, some of which may be overcome and some of which are fundamental.³¹

Unless you are living on the sun, where nuclear fusion occurs, hydrogen is not an energy source. It is an energy carrier. The basic problem is how to obtain it. Although about 40 million metric tons of hydrogen is produced annually by the oil and chemical industries, most of it is captive production used in ammonia and methanol production and refinery processes. To obtain it from water requires as much energy as can be recovered when it is burned to water, so electrolytic hydrogen is only worthwhile if cheap electricity is available. This is not wholly absurd. Technology Convergence, a Canadian company, has launched a “green” methanol process in which only 60–100 kg of carbon dioxide per metric ton methanol is produced compared with 300–700 kg in conventional plants.³² The process employs water electrolysis and partial oxidation. It offers the hope of methanol and hydrogen production in small portable plants but depends on cheap hydroelectricity.

Apart from electrolysis, the cheapest route to hydrogen (but from a nonrenewable source) is by steam reforming or partial oxidation of methane (Sections 12.4.1 and 12.4.5). Each molecule of methane gives eventually four atoms of hydrogen and one molecule of carbon dioxide with $\Delta H_{298}^\circ = -65 \text{ kJ/mol}$. The four hydrogens combust to give 967 kJ/mol. Methane combustion direct gives $\Delta H_{298}^\circ = -802 \text{ kJ/mol}$, so that 17% of the combustion energy is lost in the conversion, and the amount of carbon dioxide produced is the same. On the other hand, it is produced in a concentrated form and could conceivably be “buried” in the deep ocean or elsewhere. Other possible

hydrogen sources are methanol, ethanol, Fischer – Tropsch hydrocarbons, and low-sulfur gasoline. Methane is attractive for static use but requires a high reforming temperature. Methanol is the most attractive for automotive use. It is easier to contain than methane and can more easily be reformed. Meanwhile, the reforming process generates carbon dioxide, and the hydrogen economy combats global warming only insofar as fuel cells are more efficient than traditional power stations or internal combustion engines, thus producing less CO_2 .

There are many enthusiasts for the hydrogen economy,³³ but at present they state blandly that the hydrogen would be generated from “green” electricity, without stating how this would be obtained. Handling and storage of hydrogen presents problems – see below. The piping of gas around the country, curiously, is a nonproblem. Town gas, widely distributed in the nineteenth and twentieth centuries in the United Kingdom, consisted largely of hydrogen, and the system seemed to work well. Its replacement by natural gas after 1970 increased the energy carrying capacity of the system, but the network could revert to hydrogen with only temporary inconvenience. Meanwhile, if the hydrogen must be generated by electrolysis, one is probably better off staying with an electricity-based domestic economy.

20.3.7 Fuel Cells

The drawback of generating electricity by burning fuel and using the heat to raise steam and power a turbine is that the efficiency is limited by the second law of thermodynamics. The best thermal efficiency that can be achieved is about 33%. The use of combined heat and power (CHP) systems can nudge this into the upper 30s. Power station generated electricity is thus inevitably expensive.

A fuel cell is a device that generates electricity directly from chemical energy.³⁴ Fuel cell research has been in progress for several decades and is coming to fruition. A typical fuel cell generates about 1.1 volts at zero load, dropping to about 0.8 volt on moderate loads and then dropping rapidly at current off takes greater than 1.1 A/cm^2 . Because the voltage output is low, fuel cells have to be produced in stacks, and each unit requires separate supplies of fuel.

The attraction of the fuel cell lies in its circumventing the second law of thermodynamics. The Carnot efficiency of a heat engine operating between an upper temperature T_1 and a sink temperature T_2 is $(T_1 - T_2)/T_1$. The maximum fuel cell efficiency based on the combination of hydrogen and oxygen is the ratio of the Gibbs free energy change (ΔG°) to the enthalpy (ΔH°) change accompanying the reaction. These are shown in Figure 20.4 for $T_2 = 298 \text{ K}$. At high temperatures, the efficiency of a heat engine is higher than that of a fuel cell but, because of the need for rotary or reciprocating motion in a heat engine, there are operating costs associated with them that do not apply to fuel cells. Meanwhile, a high temperature fuel cell operating in a combined heat and power (CHP) system can achieve fuel cell efficiencies of nearly 70% and total energy efficiencies of 90%.

Some of the types of fuel cell are listed in Table 20.4 together with their operating temperatures, electrolyte, electrocatalyst, fuel, and probable mode of application. They fall into two groups characterized by low and high operating temperatures.

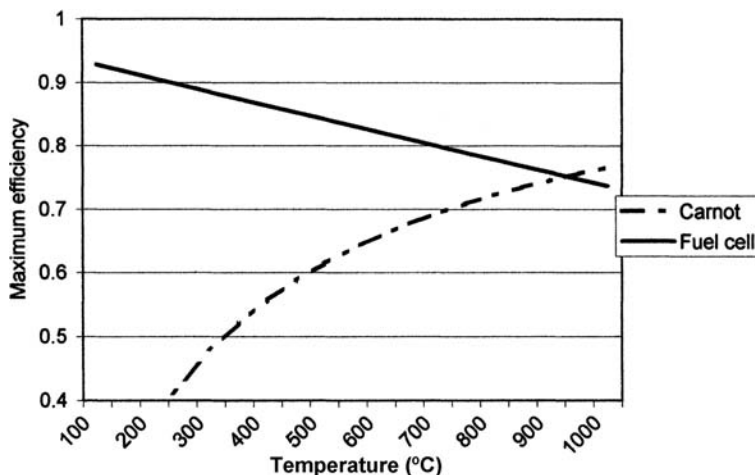
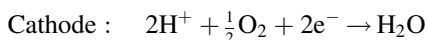
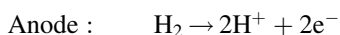


FIGURE 20.4 Carnot and fuel cell maximum efficiencies.

The low temperature cells require pure or almost pure hydrogen and are regarded as suitable for transport applications, while the high temperature systems are more suitable for stationary generation especially in CHP systems. The low temperature AFC system was used in the Gemini, Apollo, and space shuttle programs. PEMFCs are regarded as the most suitable for transport applications, having a high power density and therefore occupying relatively little space. They are also attractive as battery replacements in, for example, laptop computers, where they would operate longer than traditional batteries, cost less, and be refueled in minutes rather than hours. The structure of the PEMFC is an example of the assembly of fuel cells. It consists of platinum-based catalysts supported on carbon current collectors separated by a membrane that will conduct protons (Fig. 20.5). Hydrogen flows over one electrode, air over the other. The reactions are almost the simplest possible:



An electrolyte is required to transport the protons from the negative to the positive interface. It must have minimum resistance to proton conductivity, be an effective barrier to electronic short circuit, have low permeability to hydrogen and oxygen, and be chemically stable to hydrogen and air even in the presence of the catalyst. In addition, the membrane needs to be compact, because fuel cells produce an output of less than a volt.

The preferred material for PEMFCs at present is a *Nafion* polymer, similar to the type used in membrane cells for chloralkali production:

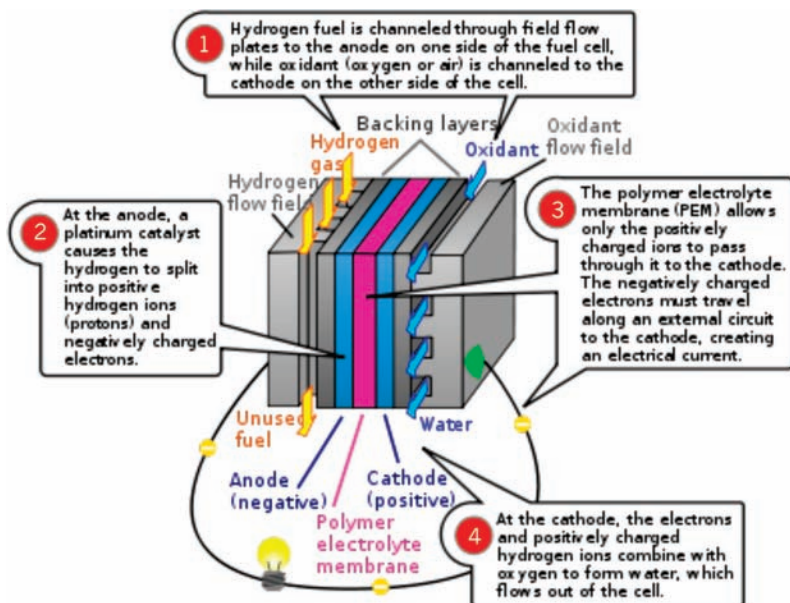
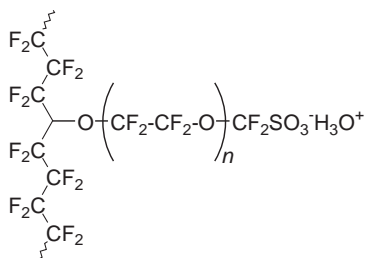


FIGURE 20.5 Proton exchange membrane fuel cell. (Source: http://en.wikipedia.org/wiki/Fuel_Cell.)



This is an ion exchange resin. If kept moist, protons can pass from one sulfonic acid site to another through nanometer-scale ionic channels.

PAFCs have been the most successful fuel cells between 1997 and 2002, when 220 commercial power plants were delivered. Typical applications lie in hospitals, army facilities, and leisure centers, where there is a suitable heat and power requirement. In the longer term, PEMFC plants are liable to prove cheaper, and SOFC or MCFC plants may provide more useful heat output and run on hydrocarbon fuels.

The MCFCs and SOFCs can operate on a range of fuels, hydrocarbons being reformed in situ on the electrodes, although some designers prefer a separate catalyst bed. They are effective in CHP installations and can operate efficiently on a smaller scale than traditional power stations.

Other types of fuel cell include the zinc – air fuel cell (ZAFC) and the proton ceramic fuel cell. The ZAFC contains a gas diffusion electrode, a zinc anode separated

TABLE 20.4 Types of Fuel Cell

Type	Abbreviation	Operating Temperature (°C)	Electrolyte and Electrocatalyst (incorporated in anode and cathode)	Electrocatalysts (incorporated in anode and cathode to promote electrode reactions)	Fuel	Uses and Comments
Alkali	AFC	60–250	At 250°C: 85% w/w/ KOH Below 120°C: 35–40% w/w retained in porous matrix (asbestos)	Nickel and noble metals	Restricted to pure H ₂ and O ₂ . Poisoned by CO formed when hydrocarbon or alcohol feeds are reformed. CO ₂ in air reacts with KOH.	Space vehicles; possible transport applications
Polymer electrolyte/ proton exchange membrane	PEMFC	80–120	Proton conducting polymer (e.g., Nafion)	Pt or Pt/Ru (more tolerant to traces of CO)	H ₂ or hydrogen-rich reformat from methanol or gasoline.	Transport; battery “replacement”
Phosphoric acid	PAFC	150–220	100% phosphoric acid in silicon carbide matrix	Pt	Steam-reformed natural gas	Medium CHP; ^a preferred design at present for stationery power generation

Molten carbonate	MCFC	600–700	Alkali carbonates in a ceramic LiAlO_2 matrix	Ni and NiO	H_2 -rich gases such as methane. Fuel contaminants less important.	Stationary power generation; large CHP
Solid oxide	SOFC	600–1000	A dense ceramic usually yttria stabilized zirconia (YSZ)	Cathode: a perovskite material such as Sr-doped lanthanum manganite, often mixed with YSZ. Anode: cermet of nickel and YSZ	H_2 -rich gases such as methane. Fuel contaminants less important.	Stationary power generation; all sizes of CHP; auxiliary power units for vehicles.
Zinc–air fuel cell	ZAFC	700	Oxygen-permeable membrane; hydroxyl-carrying ceramic solid electrolyte	Zinc anode	Zinc is oxidized to zinc oxide and regenerated by electricity. Works with H_2 or CH_4	
Protonic ceramic fuel cell	PCFC	700	Ceramic electrolyte with high proton conductivity		Hydrocarbons.	

* CHP = Combined heat and power installation.

Source: www.benwiens.com/energy3.html, *The Scientist*, 11 November 2002, pp. 28–29; N. Brandon, *Encyclopedia of Energy*, Elsevier, 2004; and N. Brandon and David Hart, *An Introduction to Fuel Cell Technology and Economics*, Imperial College, London, Occasional Paper 1. See also http://cogeneration.net/protonic_ceramic_fuel_cells.htm.

by electrolyte, and some form of mechanical separators. The gas diffusion electrode is a permeable membrane; atmospheric oxygen passes through and is converted into hydroxyl ions and water. The hydroxyl ions travel through an electrolyte and reach the zinc anode, where they react to form zinc oxide and create an electrical potential. This is similar to a PEMFC, but the refueling resembles batteries. There is a zinc “fuel tank” and refrigerator that are connected to the grid, which regenerates the metallic zinc from the zinc oxide. This is a rapid process, and, together with its high specific energy, is the advantage of this type of cell.

Protonic ceramic fuel cells (PCFCs) are a relatively new type of fuel cell and are based on a ceramic electrolyte material that exhibits high protonic conductivity at elevated temperatures. They share the thermal and kinetic advantages of high temperature operation at 700°C with molten carbonate and solid oxide fuel cells, while exhibiting all the intrinsic benefits of proton conduction in PEM and phosphoric acid fuel cells. They can be used directly with hydrocarbon fossil fuel without the need for reforming.

The improvement of the electrocatalyst is an area of intense research. Expensive platinum in a variety of forms seems to be generally favored but it has been suggested that carbon nanotubes doped with nitrogen could replace it at much lower cost. The nitrogen atoms have high electron accepting ability, which creates net positive charge on the adjacent carbons, which in turn readily attract electrons from the anode and drive the oxygen reduction reaction.³⁵ A nickel bisdiphosphine derivative can also replace the platinum catalyst. Monash University has demonstrated the use of PEDOT (see Fig. 17.14) as a cathode and, unlike platinum, it is not poisoned by carbon monoxide, frequently a contaminant in fuel cells.²⁷

The storage and extreme flammability of hydrogen present problems, especially for the low temperature cells. As hydrogen boils at only 20 K, liquefaction is an extreme option. Very high pressure reinforced plastic filament wound storage tanks have been proposed. Storage in the form of metal hydrides or in carbon nanotubes or other specialized molecular structures are topics of research, but they usually require pressure swings and/or heating to release the stored hydrogen. An alternative is to use a liquid fuel either instead of hydrogen or that can be reformed to hydrogen in an ancillary unit. Methanol is the preferred candidate and is used in the so-called direct methanol fuel cell (DMFC). The snag is that methanol oxidation at the negative electrode passes through carbon monoxide, which poisons the activity of the platinum catalysts. A further problem is that fuel cells do not respond well to sudden increases in load and they need to be accompanied, in automobiles, by batteries or supercapacitors to provide surges of power during acceleration.

In spite of all these difficulties, automobile manufacturers have built fuel cell electric vehicles in which hydrogen is either carried as a compressed gas or adsorbed on a special alloy or produced in situ by the reforming of methane, methanol, or gasoline. Daimler-Chrysler, Toyota, Honda, and BMW all have prototypes.³⁶ In 2008, Honda marketed a hydrogen fuel cell powered vehicle, the FCX Clarity, and there are other bicycles with similar technologies. Buses are a particular target in that they can all refuel at the same point and thus do not need a hydrogen distribution infrastructure.

The Brazilians launched a prototype bus in Sao Paulo in 2009. Daimler-Chrysler uniquely has demonstrated a go-cart based on direct methanol conversion.³⁷

When hydrocarbons are reformed, it is claimed that they give far less hydrocarbon pollution than when they are burned directly in an internal combustion engine. Figures of 15–20% are quoted for the efficiency of internal combustion engines for converting gasoline to energy. A variety of figures is quoted for fuel cells ranging from 35% for small fuel cells to 45% for the largest, if one starts from methane. Oxides of sulfur are low because low sulfur fuels such as methanol or desulfurized natural gas are used. NO_x emissions are low because even the high temperature fuel cells do not operate in the region where the N_2/O_2 reaction occurs. Other sources say that a fuel cell power plant will produce 20–30% less CO_2 than a conventional plant, that a reformed-gasoline powered vehicle will produce little or no reduction in greenhouse gas emissions, but that methanol will cut them by 25% and natural gas by 40%. Hydrogen from wind or solar power emits no greenhouse gases.

An impetus to hydrogen fuel-cell-powered vehicles came from U.S. President George Bush. He proposed the Hydrogen Fuel Initiative (HFI) in 2003 and followed this up with the 2005 Energy Policy Act and the 2006 Advanced Energy Initiative. The associated announcements quoted 40–65% efficiency, with a figure of 90% for CHP, but those figures started from hydrogen not methane. The project had cost taxpayers \$1 billion by 2008. In 2009, however, President Obama cut off the funds on the grounds that other vehicle technologies would reduce emissions more quickly and more cheaply. The government opinion was that hydrogen vehicles would not be practical for 10–20 years. Regrettably, all fuel cells are still substantially more expensive than fossil fuel options. Large scale production could reduce this, as could cells that did not involve precious metals, but there is still a crucial problem, frequently glossed over by the media, of economic hydrogen supply and storage.

20.3.8 Electric Vehicles

We should mention that electric vehicles running on rechargeable batteries, and hybrid vehicles with electric- and gasoline-powered engines, are already in production. The traditional lead-acid batteries are unwieldy and slow to recharge, but modern lithium batteries are improving all the time. It is likely that they will soon be able to run for a day on a single charge and then recharge overnight. This is fine for vehicles such as buses, which can return to a single charging station at the end of the day. Hybrid vehicles that use braking energy to recharge batteries and hence get more miles to the gallon are also developing. These require electricity or fossil fuels but less of them.³⁸

The snag is that batteries are made from lithium, copper, and refined silicon, which require a good deal of energy to be processed. A study has found that electric cars probably produce higher emissions over their lifetimes than petrol equivalents because of the energy consumed in making their batteries.³⁹

An electric-car owner would have to drive at least 80,000 miles before producing a net saving in CO_2 . Many electric cars will not travel that far in their lifetimes because they typically have a range of less than 90 miles on a single charge and are unsuitable for long trips. Even those driven 100,000 miles would save only about a tonne of CO_2 .

over their lifetimes. On the other hand, the batteries are improving all the time, and this study may prove over-pessimistic.

20.4 POLLUTION

Sustainability also involves issues of pollution. Are the by-products of modern living accumulating at a rate that presents a danger to future generations? Pollutants fall broadly into two categories – those affecting the global ecosystem, such as the ozone layer and the global climate, and those affecting individuals, such as carcinogenic chemicals in the environment. The latter may be subdivided into air pollution, water pollution, and pollution by solids.

Many of the pollution problems are basic to living – people burn fuel to keep warm and hence produce particulates and sulfur dioxide; they excrete waste materials. A human exhales about 1 kg of carbon dioxide per day, but stopping breathing is a drastic solution to this addition to the carbon footprint. As populations increase, the self-renewing aspects of natural ecosystems fail, and pollution may threaten health and comfort or even destabilize the environment as, for example, by deforestation. There are also numerous localized pollution problems connected with the chemical and allied industries. It is even difficult to know which chemicals are being produced. On the order of 100,000 chemicals are manufactured (Section 1.3.4). Producers are expected to provide the government with premanufacturing notice before going ahead and should submit process flow data, but the task of assessing the chemicals and their by-products in any detail is insuperable. Meanwhile, the Environmental Protection Agency monitors the release of toxic chemicals including persistent bioaccumulative toxic chemicals (PBTs). In 1995 the United Nations declared the “dirty dozen” chemicals to be PBTs, notably aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, and toxaphene. Since then, this list has grown to include carcinogenic polycyclic aromatic hydrocarbons, certain brominated flame retardants, and some organometallics such as tributyltin. The U.S. Environmental Protection Agency (EPA) includes lead, mercury, and cadmium compounds in its list of PBTs. It also rates dioxins and dioxin-like compounds not only by the amounts emitted but also by their toxicities. These values are called toxic equivalents (TEQs). They describe how toxic each dioxin and dioxin-like compound is compared to the most toxic members of the category: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin.

In 2009, 2.545 million metric tons (5.6 billion pounds) of chemicals was released to air, land, and water together with 1.530 metric tons (3.37 million pounds) of PBTs. Lead is easily the largest pollutant, accounting for about 97% of all toxic wastes. The other pollutants, classified by group, are shown in Figure 20.6. Levels have dropped but only slightly over the decade to 2009. The majority of PBTs emitted were polycyclic aromatics with the pendant groups varying from year to year but with no dramatic differences between them. The sources of the emissions are shown in Figure 20.7. The principal source of PBTs is the metal mining industry (NAICS 10).

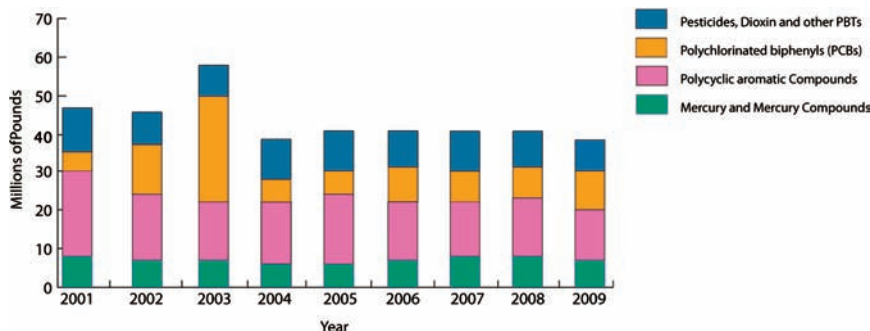
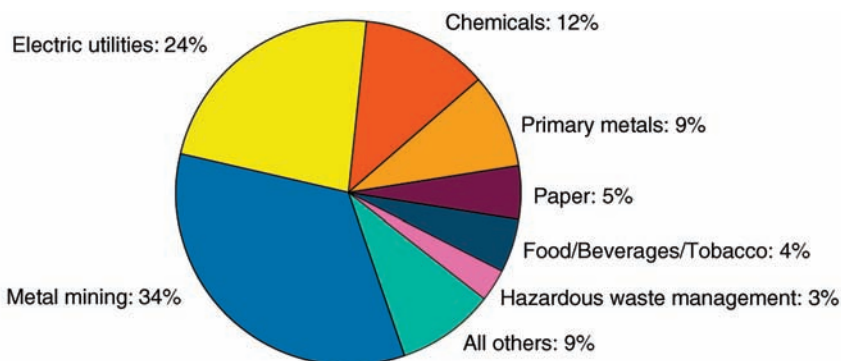


FIGURE 20.6 Total U.S. production-related waste managed nonlead PBT chemicals 2001–2009 (Source: <http://www.epa.gov/tri/tridata/tri09/nationalanalysis/overview/2009TRINAOOverviewfinal.pdf>.)

If we add the primary metals industry (NAICS 33), 41% of emissions are accounted for. Electrical utilities come second. In particular, coal burning power stations are responsible for the majority of the mercury pollution in the United States (but not in the UK; see Section 20.4.5.3). The chemical industry comes third in the emissions list and accounts for only an eighth of emissions. How are these emissions disposed of? A summary of the statistics is shown in Table 20.5. Of the 1530 metric tons, 1364 is dealt with on-site. 91 metric tons is discharged to the air, 0.20 to surface water, 1.71 somehow on land, and 0.17 injected into the ground. The chemical industry releases have been declining steadily through the 1980s and 1990s and they are rarely harmful. They decreased by 28% between 2001 and 2009, half of this decrease being a reduction in air emissions. Meanwhile, they are of the same order of magnitude as production of phthalic anhydride or o-xylene, and there is no way they can be ignored. Detailed relatively accessible statistics are produced by the EPA.^{40,41}



Total emissions = 15300 metric tons (3.37 million pounds)

FIGURE 20.7 Disposal of or other releases by industry (United States, 2009). (Source: <http://www.epa.gov/tri/tridata/tri09/nationalanalysis/overview/2009TRI-NAOverviewfinal.pdf>.)

TABLE 20.5 Waste Management in the Chemical Industry (United States, 2009)

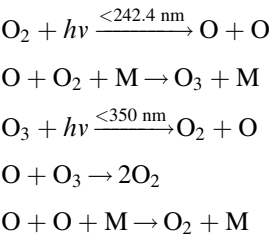
Production-Related Waste Managed: 8239.1 million pounds (3745 thousand metric tons)
• Recycled: 3262.7 million pounds (1480 thousand metric tons)
• Energy Recovery: 1195.1 million pounds (543 thousand metric tons)
• Treated: 3348.8 million pounds (1522 thousand metric tons)
• Disposed of or otherwise released: 432.5 million pounds (197 thousand metric tons)
On-site and Off-site Disposal or Other Releases: 426.3 million pounds (193 thousand metric tons)
On-site: 72.6 million pounds (33 thousand metric tons)
• Air: 157.3 million pounds (71.5 thousand metric tons)
• Water: 29.0 million pounds (13 thousand metric tons)
• Land: 48.8 million pounds (22 thousand metric tons)
• Underground injection: 137.5 million pounds (32.5 thousand metric tons)
Off-site: 54.7 million pounds (24.9 thousand metric tons)

Source: EPA.

The use of TEQs provides some balm for the chemical industry. While it is responsible for 72% of the emissions of dioxins and dioxin-like substances when measured in grams, and the primary metals industry is responsible for only 20%, when TEQs are taken into account, the figures are reversed; primary metals are responsible for 57% and chemicals for only 23%.

20.4.1 The Ozone Layer

As noted above, the surface of the earth is protected from ultraviolet radiation from the sun with a wavelength below about 360 nm by the ozone layer in the atmosphere about 20–40 km above the ground. It is maintained by a photochemical equilibrium between ozone and oxygen⁴²:



(M is any third body that carries away some of the heat of reaction.) A reduction in ozone levels allows more ultraviolet light to reach the earth, which leads to an increase in skin cancer, especially among sunbathers. It also leads to cataracts, DNA changes in marine species, and degradation of plastics.

The ozone layer was being destroyed primarily by halogen atoms generated by photolysis of chlorofluorocarbons used as aerosol propellants, refrigerator working liquids, blowing agents for foams, cleaning fluids, and solvents for the electronics industry.⁴³ Chlorofluorocarbons having no hydrogen atoms are termed CFCs and

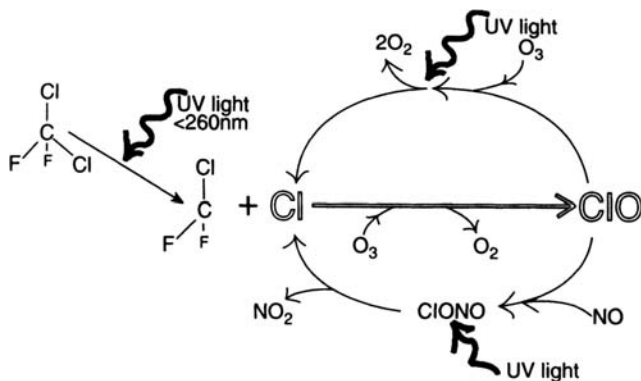
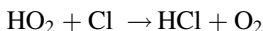
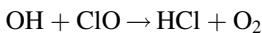


FIGURE 20.8 Destruction of ozone by halogen atoms. (Source: <http://www.nas.nasa.gov/about/education/ozone/chemistry>.)

those with hydrogen atoms are termed HCFCs. The two predominant CFCs were CCl_3F , trichloromonofluoromethane and CCl_2F_2 , dichlorodifluoromethane (known as CFC-11 and CFC-12, Section 12.2.4). They photolyze in ultraviolet light of less than 230 nm in the stratosphere to give chlorine atoms, which then participate in the cycle shown in Figure 20.8. It is estimated that one chlorine atom can degrade over 100,000 ozone molecules before it is removed from the atmosphere by the processes



Hydrogen chloride may then be removed from the stratosphere by water in which it is soluble. It is said that methane and other hydrogen-containing species including HCFCs can also convert chlorine atoms to HCl.

The potency of halogenated compounds varies and depends on the relative stability of compounds such as ClONO_2 , collectively called reservoirs, which hold chlorine in an inactive form but can be photolyzed by ultraviolet light. The reservoir compound hydrogen fluoride is so stable that fluorocarbons have no effect on ozone. On the other hand, the bromine compounds HBr and BrONO_2 are said to be 10–100 times more effective ozone depleters than the chlorine equivalents.

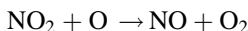
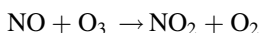
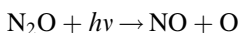
In the lower stratosphere and troposphere, oxides of nitrogen and hydroxyl radicals can also catalyze ozone degradation, but they are also able to tie up chlorine in relatively stable reservoir compounds from which they are rained out of the atmosphere.

The upshot of this was that the large-scale production of CFC-11 and CFC-12 was halted in the United States in October 1978. All CFCs and some HCFCs were designated class I ozone depleters and were rapidly phased out. The remaining HCFCs, designated class II ozone depleters, were less damaging. They were and are permitted for transitional periods and are similarly to be phased out by 2030. Hydrofluorocarbons (HFCs), containing no chlorine, appear to be industry's

replacement for refrigerators. HFCs pose no direct threat to the ozone layer and are energy-efficient refrigerants. Environmental groups argue, however, that HFCs are powerful global warming gases and damage the environment in other ways. Electronic component fabricators have replaced CFCs for cleaning with various oxygenates such as acetone and isopropanol, allied to flammability precautions. They also use microfiber polyester polishing cloth.

The hole in the Antarctic ozone layer has been getting slowly and irregularly smaller as levels of CFCs decline. The effective equivalent chlorine concentration – the measure of ozone depleting chemicals – dropped by 10% in 2008 from its peak in 1994. The World Meteorological Organization and the United Nations Environment Program jointly announced that the Montreal Protocol of 1997 was working. All the same, as a result of the exceptionally cold Antarctic winter in October 2006, the hole reached a record size. There are many factors governing climate.

Meanwhile, the decline in CFCs means that nitrous oxide emissions are now the single most important threat to the ozone layer.⁴⁴ Nitrous oxide is stable in the lowest level of the atmosphere, the troposphere, where it acts like a greenhouse gas. When it migrates to the stratosphere, it depletes ozone in the following cycle:



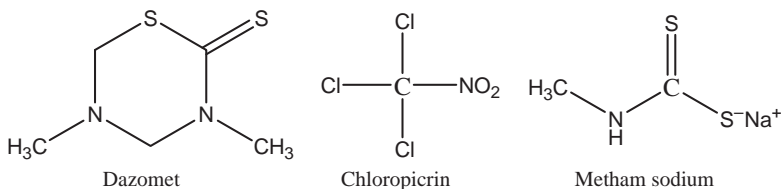
About one-third of nitrous oxide comes from human activity – primarily agriculture – and the anthropogenic portion is increasing at about 1% per year.

The above mechanisms are much simplified. There is still ignorance about many of the mechanisms governing the ozone layer, and there are arguments concerning the policies to be followed. An example of the dilemmas that are encountered is provided by methyl bromide. About 70% of methyl bromide is used as a soil fumigant. In warm regions, where termite infestation is a problem, it is used to fumigate housing and is also used on fruit and flowers, and on durable commodities such as timber.

Methyl bromide has a lifetime in the atmosphere of 1.5–2 years, and it takes 2–5 years to reach the stratosphere, so that very little arrives there. But what does arrive is very damaging. Methyl bromide was listed as a class I ozone depleter in the 1990s and it was agreed that it would be phased out by 2005.

This was all very well, but for developing nations a threat to food production was a serious matter. Banning fluorocarbon propellants in hair sprays was one thing; banning soil fumigants was another. The Montreal Treaty partners agreed to delay the compliance of developing countries with the Protocol. Methyl bromide production and use would be frozen in 2002 at average 1995–1998 consumption levels. In 2005, production would cease, apart from various exemptions. The exemptions are complicated and appear to suggest permitted production and use at 10–15% of 1991 levels, but the accompanying statement mentions “critical or emergency situations where no reasonable substitute exists either from a technical or economic point of view” or where “the non-availability of methyl bromide would cause significant harm in the relevant market.” The precise meaning that will be attached to this clause

depends on how easy it is to find effective and inexpensive substitutes, and it is not inconceivable that the whole initiative in developing countries could collapse with supplies of methyl bromide coming from countries not signatories to the Montreal Protocol. Replacements for methyl bromide are not easy to come by, although the EPA has come up with suggestions.⁴⁵ 1,3-Dichloroprene, Dazomet, chloropicrin, and metham sodium have been proposed but each has its drawbacks.



Methyl iodide is an attractive option in that it can be used with the same equipment as the bromide, and it photodegrades rapidly. Hence it is not ozone depleting, but it is expensive. In 2011 the State of California Department of Pesticide Regulation approved its use, but an appeal is under way on the grounds that it is a neurotoxin, especially dangerous to children and fetuses.⁴⁶

Numerous exemptions have been applied for in the United States, notably from tomato, strawberry, and ornamental shrub growers, and for the fumigation of ham/pork products. Treatment of solid wood packaging (forklift pallets, crates, bracing) may also be exempted.⁴⁷ It is unclear where and how many exemptions have been granted but annual world production of methyl bromide by 2008 had dropped to perhaps 15,000 metric tons from a peak of 66,000 metric tons.⁴⁸

The contribution of the chemical industry to methyl bromide pollution is not clear. It has been suggested that some 42,000 metric tons/year of the methyl bromide used for soil fumigation before the ban was consumed by soil bacteria and presumably converted to harmless bromides.⁴⁹ Furthermore, marine organisms (macroalgae) produce tens of thousands of metric tons per year of organobromines and probably 80% of atmospheric methyl bromide is of natural origin.⁵⁰ Other workers provide figures as low as 70%, but combination of any of these figures with the Greenpeace figure of 3% (itself an upper limit) for the contribution of methyl bromide to ozone depletion still leaves less than 1% attributable to soil fumigation. Is this worth the disruption of agriculture?

Some countries have signed the Montreal Treaty unwillingly (China and India) and others have done so conditionally depending on financial recompense (Brazil). There is a Chinese venture into bromine production. This may be part of an industrialization program, but it could also be a preemptive measure should external bromine sources dry up. After all, the United States and Israel (the world's two major bromine producers) and 161 other countries have signed the Treaty. Meanwhile, the overall ozone protection program has apparently been a success, in that ozone depleting gases have decreased by 11% between 1994 and 2008. The decrease has been greatest in the Northern Hemisphere, suggesting that the reduction in anthropogenic ozone depleters has been responsible for the decrease.

20.4.2 Trace Chemicals

A central worry of the environmentalists is the presence of trace chemicals in the environment that are known to be or, on the precautionary principle, might possibly be detrimental to health. Some of these have already been banned as a result of their concerns. Lead has been removed from gasoline and benzene levels have been minimized. Mercury pesticides have been banned in paint; DDT use has been heavily restricted. There is a continuing review in developed countries of the danger from human-made chemicals. A selection of topics is discussed below.

20.4.2.1 Pesticides

Pesticides have been a prime target for environmentalists, mainly because such materials may appear in our food and may thereby lead to cancer. While the causes of cancer are difficult to identify specifically, Richard Doll, who first demonstrated the link between smoking and lung cancer, estimated in 1981 that 35% of cancers were diet induced. Meanwhile, we all have to go on eating, and society should be cautious that materials dangerous to health are excluded from diet. Pesticides are divided into four groups – chlorinated, hydrocarbons, organophosphates, carbamates, and chlorophenoxy acids. Chlorinated hydrocarbons (Section 9.6) are the most persistent, with a lifetime in the environment of several years. They are absorbed by creatures a long way down the food chain and, by the time they reach our dinner plates, they have already become concentrated with respect to their level in the environment generally.

The mosquito eradication program on Long Island, New York, showed levels of DDT in sea water of 3 ppm, in the fat of plankton of 0.04 ppm, in the fat of minnows 0.5 ppm, in the fat of needlefish 2 ppm, and in the fat of cormorants and osprey 25 ppm. People contained similar levels to birds of prey. While the adverse effects of DDT on birds have been amply documented, there are still doubts as to whether it actually thins eggshells. It is worrying to reflect on the persistence of DDT in human tissue, but reassuring to record that no demonstrable ill effects of organochlorine insecticides on humans have been detected in spite of levels of up to 600 ppm being found in workers in a DDT factory. Meanwhile, the use of chlorinated hydrocarbons was forbidden or discouraged to the extent that, by 1985, usage in developed countries had been restricted to about 5% of its peak value.

Organophosphorus pesticides biodegrade in a matter of months. Parathion is the most persistent of the widely used materials with a typical half-life of 120 days. It has probably been responsible for more deaths than any other pesticide. It has high mammalian toxicity and is absorbed through the skin, inhaled, or swallowed during spraying operations. Exposure to organophosphorus insecticides is dangerous, but the fact that they are less persistent means that, despite their constant monitoring as part of public health, they are only peripherally part of the sustainability debate. Their use is restricted both to protect agricultural workers and to prevent even small pesticide residues persisting on food products. The same applies to other pesticides.

20.4.2.2 *Nonpesticide Lipophiles*

Many pollutants owe their toxic effects to their accumulation in the body. They are lipophilic and biochemically rather inert. The body is capable of dealing with some lipophiles. Benzene and toluene are both lipophilic, but benzene has no functional group that can be attacked by an enzyme. Toluene, on the other hand, is enzymatically oxidized to benzoic acid, which subsequently couples with either glucuronic acid or glycine to give benzoylglucuronic acid or hippuric acid, both of which are readily excreted. Thus benzene is a carcinogen while toluene is nontoxic.

The classic group of lipophiles, banned as long ago as 1976 (The Toxic Substances Control Act), were the polychlorinated biphenyls. They were used in industry mainly as electrical insulators in transformers and capacitors. A domestic application was in the capacitors in fluorescent light ballasts. Polychlorinated biphenyls take several decades to degrade and are still produced inadvertently in small quantities in plants where organochlorines are made (Fig. 20.6). Like the chlorinated hydrocarbon pesticides, they accumulate in fatty tissue and are damaging to the animals high up the food chain, that is, to humans.

The majority of organochlorine lipophiles have been phased out. Various organobromine compounds are still in widespread use. A range of polybrominated compounds – polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and tetrabromobisphenol A – are used to prevent or deter fires in electronic devices (mainly television sets and electronic components), furniture, and textiles. PBDEs have been found in the body fat of many wildlife species, including sperm whales in the Atlantic Ocean and in mothers' milk in Sweden. The pentabromo and octabromo compounds have been banned, but there is still widespread use of the deca compound, amounting to about 40,000 metric tons/year, although other sources claim 200,000 metric tons.⁵¹ There are no allegations against tetrabromobisphenol A because it is chemically bound as a comonomer in the epoxy resin of printed circuit boards, which is its principal application.

The evidence raises a series of questions. Toxicological studies indicated that large doses of the flame retardants given to neonatal mice hindered their intellectual development, but there have been few reports of ill effects on humans, even those working in a television dismantling plant, who had 70 times the usual levels of brominated compounds in their fat. There are questions as to the transport of the compounds. They are involatile and insoluble. Whales do not watch television, nor are discarded television sets dumped at sea. There are suggestions that the brominated compounds may originate naturally from marine organisms, but that too is unsubstantiated.

A third set of lipophiles is the plasticizers for poly(vinyl chloride), of which dioctyl phthalate (usually di-2-ethylhexyl phthalate) is easily the most widely used. In addition to softening plastics, it is used in cosmetics and as a replacement for polychlorinated biphenyls as a dielectric fluid in capacitors. Like the brominated fire retardants, it is insoluble and involatile but, like other lipophiles, it accumulates in fatty tissue. About 363,000 metric tons/year (800 million pounds) enters the environment in hoses, pipes, rubbers, and plastics. It adheres to soil but is rapidly degraded in

water. In the short term, exposure causes mild gastrointestinal disturbances, nausea, and vertigo. In the longer term, it is said to damage the liver, testes, and respiratory function and “may reasonably be anticipated to be a carcinogen.” The campaign to ban dioctyl phthalate has been in progress since the 1950s, showing persistence of a different kind from that of chemicals. In 1974, the Safe Drinking Water Act limited permitted concentrations in drinking water to 6 ppb and it was subsequently withdrawn from use in babies’ pacifiers. It has now largely been phased out from children’s toys. The FDA permits use of di-2-ethylhexyl phthalate-containing packaging only for foods that primarily contain water. In 2002 the European Commission proposed a ban on phthalates in cosmetics on the grounds that they might cause genital abnormalities.

Male reproductive development in male laboratory animals is acutely sensitive to some phthalates. Several studies have shown associations between phthalate exposures and human health, although no causal link has been established. Endocrine disruption apparently occurs through interaction with the androgen receptor. Phthalates are anti-androgens, and their interaction can produce a diversity of impacts on the developing male reproductive tract. For example, dibutyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP) produced dramatic changes in male sexual characteristics of rats when exposure took place in utero, at levels far beneath those of previous toxicological concern. Pregnant women’s exposure to phthalates has adverse effects on genital development in their male children.

EPA initiated rulemaking in Autumn 2010 to add the eight large-tonnage phthalates to the Concern List as chemicals that present or may present an unreasonable risk of injury to health or the environment.⁵² The EPA website www.epa.gov lists numerous other chemicals that it monitors, and a comprehensive attack on all synthetic chemicals will be found in a recent book by Cranor.⁵³

20.4.3 Air Pollution

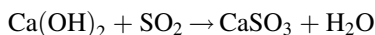
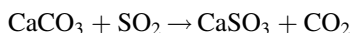
Air pollution has been tackled more vigorously by legislators than almost any other form of pollution. Laws to limit smoke from coal burning were passed in England in 1273. Queen Elizabeth I stayed away from London in 1578 because of the “noysomme smells of coal smoke” and, in 1661, John Dryden, the diarist, addressed a pamphlet to King Charles II describing the evil from smoke as “epidemicall” and a danger to health.⁵⁴ He suggested that factories using coal should be moved further down the Thames Valley and a green belt of trees put around the center of the city “to rid London of the columns and clouds of smoke which are belched forth from the sooty throates of [those shops] rendering [the city] in a few moments like the picture of Troy sacked by the Greeks or the approaches of Mount Hecla.” (Mount Hecla is a still-active Icelandic volcano.)

Meanwhile, the chemical nature of air pollution in the developed world changed entirely in the middle of the twentieth century, although it has remained unchanged in much of the third world.⁵⁵ The EPA has a website where one can follow one’s favorite pollutant.⁵⁶

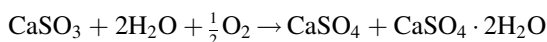
20.4.3.1 Sulfur Dioxide Particulates

Air pollution is mainly the result of combustion processes. Cigarette smoke, where a person directly inhales the combustion products, is the most dangerous air pollutant known. Other traditional combustion processes produce particulates (smoke), sulfur dioxide, and minute amounts of polycyclic hydrocarbons. Some of these polycyclics are known to be carcinogenic, but we know of no solid evidence linking their presence in the air to cancer. Under humid conditions, the sulfur dioxide may react further to give sulfuric and sulfurous acids and sulfates. They also interact with the particulates to give the sulfate aerosols that made up the traditional London fogs. These irritate the lung and exacerbate existing respiratory conditions. About 4000 people died as a direct result of the great fog of London in 1952, which precipitated the Clean Air Act of 1956. Sulfur dioxide (plus nitrogen oxides) also leads to acid rain, which attacks vegetation and destroys fish life in lakes.

Legislation in many developed countries limited the use of solid fuels and the emission of smoke, and this has reduced air pollution of that kind. Countries with cheap and/or indigenous coal reserves retrofitted flue gas desulfurization units to their coal-fired power stations. There are a number of desulfurization methods, but four-fifths of the installations worldwide use limestone (CaCO_3), lime (CaO), or seawater to scrub the exit gases to give calcium sulfite:

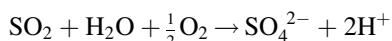


The calcium sulfite can be oxidized with air:

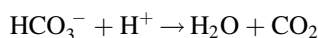


The end product is a high quality calcium sulfate dihydrate (gypsum). The process is more complicated than it sounds because of the need to keep the exit gases flowing up a chimney and to get the sulfate, which can be used in plasterboard, rather than the sulfite. In Japan, there was a problem because the supplies of high quality sulfate threatened to put out of business the traditional calcium sulfate producers, who obtained it as a by-product of the manufacture of phosphate fertilizer from phosphate rock and sulfuric acid. The government's ingenious response was to double the thickness of plasterboard required in new buildings.

Seawater is naturally alkaline and absorbs water and oxygen to give sulfate and carbon dioxide:



The hydrogen ions react with bicarbonate in the seawater to give carbon dioxide:



Flue gas desulfurization was emphasized in the United States in the 1990s and an EPA fact sheet provides technical details.⁵⁷ Its importance in Europe has been much diminished by the availability since the 1970s of natural gas from the North Sea and, since the 1980s, from the former Soviet Union. Natural gas is a clean and easily handled fuel, and the size of the Russian reserves has muted criticism that it is a mistake to use an attractive material for chemical and domestic use for such a mundane purpose as electricity generation. In China and India, however, coal is the fuel of choice and in 2008 it was the fastest growing fuel for the sixth successive year.

Sulfur dioxide/smoke pollution remains a problem but one that is being tackled. In the United States, the overwhelming majority of sulfur dioxide pollution comes from coal and oil burning and metal smelting, but some comes from volcanoes.⁵⁸ Between 1980 and 2008, average levels (measured at 141 sites) decreased by 71%. This is illustrated in Figure 20.9, which shows average levels and the upper and lower deciles – 10% of sites have higher and lower levels than these lines; the national standard level is 0.03 ppm.

In Western Europe, coal burning is less prevalent than in the United States, and effort is being put into desulfurizing gasoline and diesel fuels. In 2002, the European parliament decreed that by 2009 ultralow sulfur diesel (<10 ppm sulfur)(ULSD) be standard, a target that appears to have been met.⁵⁹ The United States mandated ULSD with less than 15 ppm sulfur from 2007, with a few exceptions where a slower transition was permitted. The production of ULSD is not without problems. Certain sulfur compounds in diesel are resistant to removal by the conventional hydrodesulfurization processes, the most refractory being 4,6-dimethyldibenzothiophene. By “deep” hydrodesulfurization, with a more active catalyst and more extreme conditions, this may react directly to 3,3'-dimethylbiphenyl:

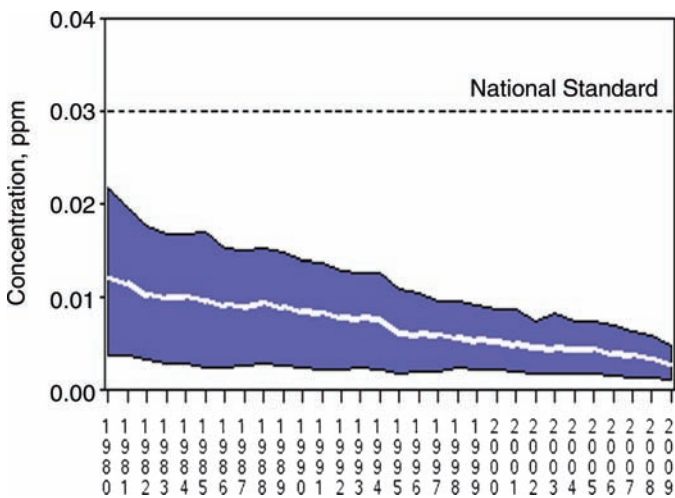
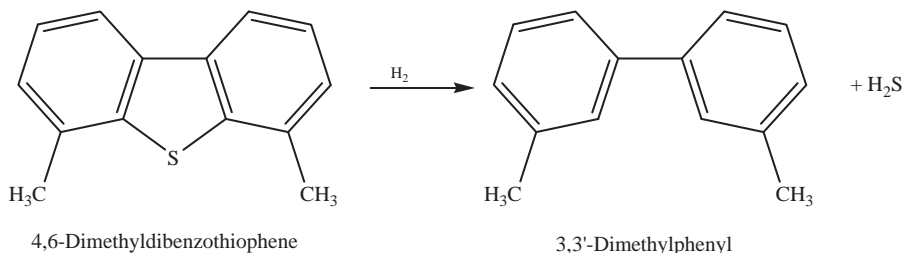


FIGURE 20.9 Sulfur dioxide pollution 1980–2009.



It may also be reduced via cyclohexyl and dicyclohexyl intermediates.⁶⁰

Sulfur reacts with nickel in engine cylinder walls to give a eutectic with lubricating properties, and its removal reduces engine lubrication. The desulfurization process also reduces the aromatics content and the naturally occurring lubricants in the fuel. To manage this change, the regulatory body, the ASTM, adopted the lubricity specification defined in ASTM D975.

These improvements come not only at an economic cost⁶¹ (the U.S. refining industry claims that the new standards involved costs of \$8 billion) but also have an environmental price. The production of entirely “zero sulfur” fuels in Europe will increase refinery carbon dioxide emission by 5% because of the additional energy required, equivalent to about 4.6 million metric tons/year of carbon dioxide, to make its contribution to global warming.

Sulfur dioxide pollution remains serious in the developing world, and also in Eastern Europe, where cheap and readily available soft coal or lignite are traditional fuels. In low-technology grates, coal combustion is better described as destructive distillation and is only slightly better than burning camel dung in a tent. The health consequences are not trivial. In the United States in 1995, 9% of deaths were attributed to respiratory disease arising from combustion-related air pollution. In China, where coal is extensively used as a domestic fuel, the proportion was 21.8%. Chinese output of sulfur dioxide reached 25.5 million metric tons in 2005, a 27% increase since 2000 and equivalent to U.S. emissions in 1980.

Thus the Chinese economic “miracle” comes at a price. The president of Shell Oil, John Hofmeister, records that during a visit to Beijing in 1996, he noticed that visibility was only about 100 yards (90 m).⁶² His host told him that he had taken his children to see the Great Wall of China and, as they got out of the car, they began to cry; they thought something was terribly wrong because the sky was a brilliant blue. Illegal forest burning in Indonesia has a similar effect in Singapore and Malaysia and, of course, there is a problem with photochemical smog in large U.S. cities, although something has been done about this (see below).

It is ironic that sulfur dioxide, while a health threatening pollutant and precursor of acid rain, also mitigates the greenhouse effect. Sulfate aerosols formed from it reflect sunlight back into space, and their removal increases global warming. Sulfur dioxide in the stratosphere absorbs UV light and prevents it reaching the earth, and various sci-fi schemes have been produced to transport the gas to this height.

20.4.3.2 Automobile Exhaust Emissions

The problems of pollution from coal burning, typified by the London fogs before 1960, were superseded by those from gasoline burning. In the United States, 77% of carbon monoxide emissions arise from transportation as do 49% of nitrogen oxides, 40% of volatile organic compounds, and 32% of carbon dioxide. Los Angeles smog replaced London fog in the public perception. They differed diametrically in that smog was associated with warm and dry rather than cold and damp weather, and it had oxidizing rather than reducing properties. Smog was formed in many cities, but it was particularly bad in Los Angeles, because the pollution was confined by meteorological inversions above the city. The damaging materials in smog are oxides of nitrogen (lachrymatory and causing pulmonary edema at higher concentrations), ozone, and peroxyacyl nitrates (PANs) (vegetation killers; ozone causes lung damage). Figure 20.10⁶³ shows the concentrations of the main pollutants during a typical Los Angeles day in the 1970s, before catalytic converters. Early in the morning, background levels of hydrocarbons, nitrogen oxides, and ozone are low. Automobile activity starts at 6 a.m., and nitric oxide and unburned or cracked hydrocarbons increase. Nitrogen dioxide reaches a peak in mid-morning but subsequently decreases in favor of ozone, which reaches a peak mid-afternoon. There is also a buildup of aldehydes, nitro compounds, and other partially oxidized species, together with aerosols containing nitric and sulfuric acids and related materials.

The smog model given in B. G. Reuben and M. L. Burstall, *The Chemical Economy*, Longman, London; 1973, p. 487, now seems embarrassingly dated. The change has come about because the development of atomic titration techniques has enabled the rate constants of hydroxyl radical reactions to be determined, and they dominate the modern mechanism.

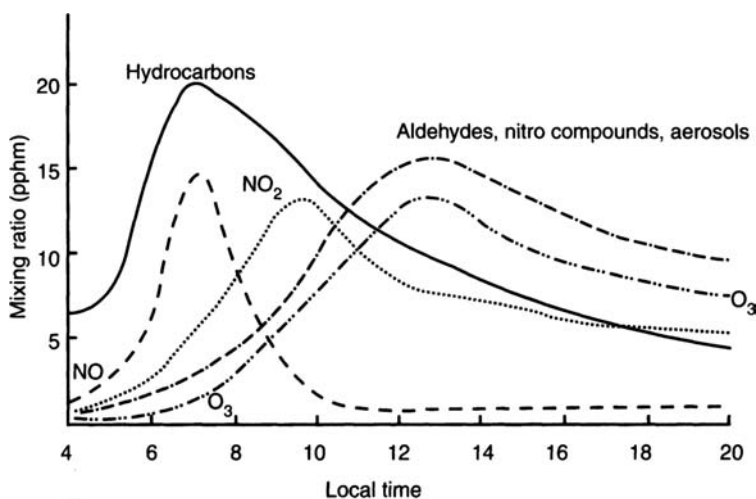


FIGURE 20.10 The typical mixing ratio profiles as functions of time of day in the photochemical smog cycle.

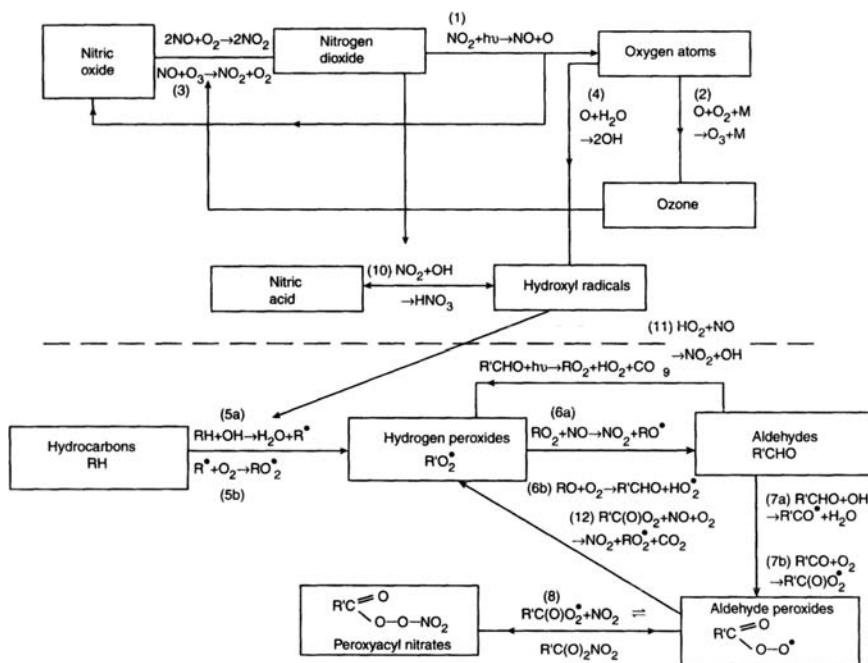


FIGURE 20.11 Los Angeles smog cycle.

Smog formation starts with the production of nitric oxide in automobile engines (Fig. 20.11). This, in itself, is an unlikely process. The reaction $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ has $\Delta H_{298}^\circ = 207 \text{ kJ/mol}$ and $\Delta S_{298}^\circ = 24.8 \text{ J/deg/mol}$, so it is thermodynamically slightly unfavorable with a very high activation energy, but nitric oxide is actually formed in small quantities at the high temperatures in an internal combustion engine. If emitted in the exhaust gases, it is oxidized by atmospheric oxygen to the brown gas nitrogen dioxide (NO_2). This is a slow termolecular process. Nitrogen dioxide absorbs strongly between 300 and 400 nm, wavelengths abundant in sunshine. The products are nitric oxide and oxygen atoms, and the latter go on to generate ozone that can react with nitric oxide to regenerate nitrogen dioxide and oxygen. The oxygen atoms can also react with water to give hydroxyl radicals, which can interact with nitrogen dioxide to give nitric acid. There is thus a complete cycle involving nitrogen- and oxygen-containing molecules, shown in the upper section of Figure 20.11. It would lead to a steady but low concentration of ozone and much lower concentrations of nitrogen dioxide than are actually found.

It is the presence of hydrocarbons and aldehydes that makes the difference. They are attacked by hydroxyl radicals to give hydrocarbon radicals, which in turn give hydrocarbon peroxides and then aldehydes. The aldehydes give aldehyde peroxides and then peroxyacyl nitrates (e.g., PANs). Any volatile organic compounds discharged into the atmosphere from other sources usually also interact with hydroxyl radicals and lose a hydrogen atom to give a free radical. The reaction scheme in Figure 20.11 is much simplified and ignores sulfate and nitrate aerosols and many

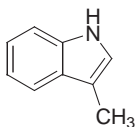
gaseous chemical species. A state-of-the-art model has 88 chemical species and 178 reactions.

The smog problem was tackled in the United States by legislation requiring catalytic converters to be fitted to automobiles to oxidize hydrocarbons and carbon monoxide while reducing nitrogen oxides (Section 18.6.1). In 1979, the Department of the Environment set an upper limit for ozone of 0.12 ppm average over a one hour period, and in 1997 this was reduced to 0.08 ppm average over an eight hour period, the reduction to be achieved by 2004. There were also fresh limits on the emission of particulates of less than 2.5 μm from heavy-duty diesel truck and similar vehicles and on emissions of volatile organic compounds. The surface coating industry switched in part to water-based or solvent-free formulations. In other areas, of which Singapore is perhaps the most widely publicized, the pollution problem continues. The United States is the largest automobile market in the world, but catalytic converters are now fitted to automobiles worldwide.

As a result, pollution levels in Los Angeles and some other American cities have dropped in recent decades. The number of Stage 1 smog alerts in Los Angeles has declined from over 100 per year in the 1970s to almost zero in the new millennium. In spite of this, the 2006 and 2007 annual reports of the American Lung Association still ranked the city as the most polluted in the country with short-term and year-round particle pollution. In 2008, the city was ranked the second most polluted and again had the highest year-round particulate pollution.⁶⁴ With pollution still a significant problem, the city continues to take aggressive steps to improve its environment.

20.4.4 Water Treatment

Domestic sewage is a very dilute liquid. Strong sewage (urban sewage undiluted by rainwater) contains only about 500 ppm of impurities. Untreated, however, it leads to odor, spread of water-borne diseases such as cholera, pollution of water courses, and the death of aquatic life. Sewage is a powerful reducing agent and its decay involves the reduction of sulfate ions by organic material in the sewage to give hydrogen sulfide and mercaptans. The breakup of proteins and other nitrogenous matter in the sewage leads to amines, which mix with unpleasant nitrogenous compounds already present in the sewage (such as skatole, which gives the smell to feces) to accentuate the odor from the sulfur compounds.



Skatole

The methods of treating wastewater have been standard for much of the past century, even though the traditions of dumping wastes in the sea or a river have been hard to overcome.⁶⁵ Wastewater is carried through sewers to a treatment plant, where it is screened to remove large solid objects. It is then sent to a settling tank where a

sludge deposits, possibly with the help of flocculating agents, leaving a supernatant “clear effluent.” If land is reasonably cheap, the clear effluent is sprinkled via a rotating arm over a trickling filter – a bed filled with pieces of broken rock 5–10 cm in diameter, which have become covered with biological growth – and the organic compounds are oxidized aerobically to carbon dioxide, water, and nitrites/nitrates.

The activated sludge method uses a tank with a spinning cone on top. This throws the clear effluent out in a spray and aerates it thoroughly. The liquid in the tank is inoculated with microorganisms similar to those in the trickling filter, and a similar oxidation process occurs. The activated sludge method occupies less space, hence is more suitable where land prices are high. On the other hand, it requires more maintenance. It has high electricity costs, whereas the rotating arm in the trickling filter is driven by the effluent being pumped out of the holes in its side.

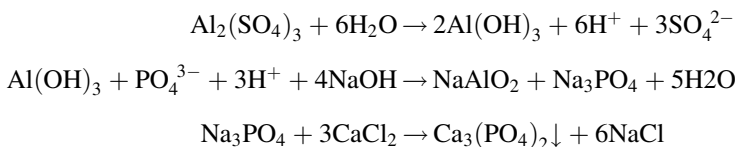
Depending on where it will finally be discharged and how it will be used, it may be necessary to disinfect the effluent. Native bacterial populations feed on the organic contaminants, and the numbers of disease-causing microorganisms are reduced by natural environmental conditions. If this is inadequate, the effluent is chlorinated. The disadvantage is that the chlorine also reacts with trace organic material to give lipophilic and possibly toxic organochlorine compounds. There are still problems in that very low levels of specific contaminants have been detected in wastewater, including hormones from animal husbandry and human contraceptives, and synthetic materials such as phthalates that mimic hormones in their action. These and other trace residual materials can have an unpredictable adverse impact on the plant and animal life and potentially on humans if the water is reused for drinking.

We return to the treatment of sludge from the settling tank. It is generally treated by anaerobic oxidation, in which it is maintained in a closed tank where it putrefies to methane and carbon dioxide. The digested sludge has no odor and dries easily but has no value as a fertilizer. The methane, however, can be used to make the sewage plant independent of outside sources of energy. Various municipalities, notably in Sweden, claim to be able to export methane and/or electricity, but once the energy costs of a sewage plant have been met, there is little if any surplus. Whatever the media may say, this technology is not new and one of us (BGR) worked on a sewage plant that generated methane in 1953.

An early problem with synthetic detergents is that they were based on branched chain dodecanes and nonanes (Section 6.3). They were not degraded by the microbiological treatment and passed into waterways to cause foaming at waterfalls and weirs. The substitution of straight chain materials reduced the problem, and biodegradability is now a key requirement for detergents.

A second problem arose with sodium tripolyphosphate, a so-called builder, added to detergent formulations to sequester polyvalent metal ions in hard water. The polyphosphate also passed unchanged into rivers and lakes. Phosphates are plant nutrients and, in their presence, blue-green algae may grow at an explosive rate and cover large areas of surface. The algae underneath each fresh growth rot and extract oxygen from the water. Fish die and the ecological balance is upset. The phenomenon is called eutrophication. Various solutions to the problem were implemented. Some zero-phosphate detergents were marketed; levels of phosphate in others were

reduced; alternative builders were employed such as zeolites. Tertiary treatment of sewage was also practiced. One method is to add aluminum sulfate as a coagulant and then calcium chloride:



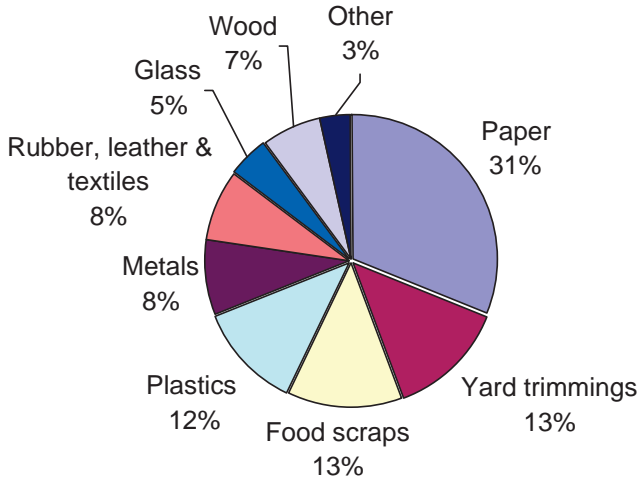
The calcium phosphate is then filtered off. An alternative precipitant is iron sulfate, prepared by reaction of scrap iron with sulfuric acid. Iron phosphate is precipitated. Both these methods help to break colloids in the sewage and aid precipitation of sludge at the sedimentation stage.

20.4.5 Solid Wastes

Disposal of solid wastes is another area where there is a threat to the environment. Industry (especially the chemical and metallurgical industries) produces gaseous, liquid, and solid wastes that may be toxic or hazardous or both. The range of these is so wide, however, that there is no general method of disposal and the reader is referred to specialist publications. Municipal solid wastes present more general problems. Both are regulated in the United States by the Office of Solid Waste under the Resource Conservation and Recovery Act, although a few wastes such as animal, medical, and radioactive wastes are controlled by other federal agencies.

Municipal solid wastes – trash or garbage – have grown in the United States from 88.1 million metric tons/year (2.7 pounds/person/day) in 1960 to 249.6 million metric tons (4.5 pounds/person/day) in 2008. This figure, however, has not increased since 1990. The nature of the wastes has changed since earlier in the century. In the days of open fires, much of the garbage would be burned, and the food wastes possibly composted. Packaging materials were few and plastics nonexistent. Domestic waste consisted largely of clinker and ashes, which could be compacted to a stable structure. In some regions, controlled tipping of these solids produced usable land.⁶⁶ Modern wastes have a totally different composition, shown in Figure 20.12.⁶⁷ The dominant material is paper – not only newspapers but advertisements, promotional material, and packaging. Food wastes are about one eighth of the total. This figure compares with over 40% in most Mediterranean countries, reflecting that American foods come ready washed and often ready prepared. The level of plastics reflects shopping habits and the ubiquitous plastic bags and food packaging, even though each bag weighs only 5–10 g. The “other” category includes materials such as paint, cleaners, used lubricating oils, pesticides, and batteries that could present toxic hazards.

The core economic problem at the heart of waste disposal is that the cheapest way to get rid of waste is to dump it. The argument that land prices will be so high near a city as to make landfill uneconomic is not viable.⁶⁸ The presence of a landfill will



USA 2008, before recycling, total 249.6 million tons

FIGURE 20.12 Municipal solid waste (United States 2008).

reduce land values around it but, even at standard land prices, purchase of a landfill site, except perhaps right in a town center, is still the most economic option, although it would be forbidden by zoning and related regulations.

Dumping under controlled conditions is given the dignified title of landfill. The main cost is shipping the waste to the landfill site. The drawbacks are numerous. Solid waste is generated principally in cities, and transport costs mean that one needs to purchase a landfill site on the edge of a city or not too far out. Inevitably the city then expands past the site, and there is immediately a problem with amenity, land values, visual pollution, and so on. There is also the problem that rain trickling through the waste can contaminate groundwater. In addition, even in thinly populated countries, one runs out of holes in the ground where waste can be dumped. Dumping at sea is forbidden under various international agreements. Whatever the economic analysis, political pressures in developed countries mean that municipal waste cannot merely be dumped. What are the options? The Environmental Protection Agency offers the following hierarchy.

20.4.5.1 Waste Prevention

Like saving energy, waste prevention is an attractive option if only one can persuade people to cooperate. Two-sided copying of paper, backyard composting, reduction in packaging, and charging for plastic bags at supermarkets are all possibilities. Those with an economic spur have the greatest chance of success, but legal methods are also possible. From January 2010, Minnesota state law decreed that yard waste put out for curbside collection must use compostable bags.

20.4.5.2 Recycling

In 2008, Americans recovered about 61 million metric tons of waste, excluding composting, by recycling it. Composting recovered another 22.1 million metric tons. About 32 million metric tons as burned and energy recovered, for example, to generate electricity (about 13%). Subtracting out what was recycled and composted, 3 pounds per person per day of waste was either burned, with energy recovery, or sent to landfill. Recycling has been a modest success. It has risen from 9.6% of solid waste in 1980 to 33.8% in 2009, while landfill has dropped from 88.6% to 54.2%. This impressive statistic, however, conceals the fact that the total waste has decreased only fractionally from 134.4 to 131.9 million metric tons.

Table 20.6 indicates that automobile batteries achieved a 95.7% recycle rate, paper 74.2% (a recent large increase), and yard trimmings (grass cuttings), through composting, 59.9%. Recycling requires a degree of householder-led segregation of garbage, but householders seem prepared to carry out a limited degree of sorting. It has been suggested in the United Kingdom, which has the worst recycling record in Western Europe, that people might be charged by weight for the disposal of unsorted garbage. There have even been suggestions about the inclusion of computer chips in garbage bins to check weights of waste and charge for its disposal. Once the waste has been collected, ferrous metals can be separated by magnetic methods and light materials – paper and plastics – can be separated from heavier ones – glass and other metals – by air classification. All this comes at a cost, and the cost in countries where labor is expensive and recycling is more likely to be adopted is much higher than in developing countries where labor is cheap and, indeed, where the very poor frequently sort through garbage heaps voluntarily in the hope of finding something of value. There is also an environmental cost attached to recycling in the sense that recycling of paper results in trace organochlorine compounds in water supplies (Section 19.7).

Europe is a more crowded continent than North America, and the European Union is increasing the range of materials that cannot be dumped. Refrigerators have already been declared hazardous waste, especially those containing chlorofluorocarbons.

TABLE 20.6 Recycling Rates of Selected Materials (United States, 2009)

Material	Percentage
Automobile batteries	95.7
Office-type paper	74.2
Steel cans	66.0
Yard trimmings (grass cuttings) composted	59.9
Aluminum beer and soft drink cans	50.7
Tires	35.3
Glass containers	31.3
HDPE white translucent containers	28.9
PET bottles and jars	28.0

Source: U.S. Environmental Protection Agency (<http://www.epa.gov/osw/nonhaz/municipal/pubs/msw2009-fs.pdf>).

There has been legislation on other electrical waste. Local authorities have to separate electronic items (television sets, video recorders, personal computers, children's toys, etc.) from other rubbish, take out any hazardous chemicals, and arrange for the dismantling and/or disposal of the remainder. Companies and members of the public have the option of returning their old goods to retailers when they buy new ones.

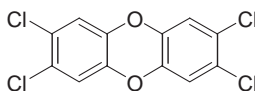
20.4.5.3 Combustion/Incineration

Burning municipal solid waste can reduce the waste by 90% in volume and 75% in weight. The heat output can be used to generate electricity and, as metals must first be separated, their sale contributes to the economics. Thus 12.6 percent of U.S. municipal solid waste was disposed of in this way in 2008, down from 16% in 2000, possibly reflecting the reluctance to increase carbon dioxide emissions.

The disadvantages are that incineration has high capital and operating costs. Because of the variability of input, there are numerous solids-handling problems together with high maintenance requirements and lack of reliability of equipment. Inefficient plant operation causes emission of odor, smoke, and pollutants. Generation of wastewater from residue quenching can lead to air and water pollution and disposal of the residue, much reduced in volume though it is, produces other problems.

Combustion inevitably leads to emission of carbon dioxide. Air pollutants emitted from incinerators are mainly smoke, odors, fly ash, sulfur, nitrogen oxides, and hydrogen chloride. Some of these can be removed by scrubbing the exit gases; others by filters. Regulations call for waste to be exposed to a temperature of at least 980°C for at least 1 second. If combustion is inadequate, flue gases may contain black smoke, partially combusted organics and carbon monoxide. Greenpeace rejects incineration as a method of waste disposal and has claimed that incomplete combustion of chlorinated organics produces airborne dioxins, furans, polycyclic aromatic hydrocarbons, hydrogen chloride, and heavy metals.

Dioxin itself has the structure



It is produced as a by-product in the manufacture of chlorinated phenols and phenoxy herbicides, chlorine bleaching of paper pulp, and combustion of chlorine-containing wastes (Section 9.1.5). It is said to be one of the most poisonous substances known, and animal tests certainly support that conclusion. Congenital malformations in laboratory animals subjected to dioxin were reported as early as 1969. The effect on humans is less well documented, but one would expect the material to be a carcinogen. Industrial workers exposed to it have developed chloroacne, porphyria cutanea tarda, and porphyria cutanea tarda. The Seveso accident in 1976, in which 2 kg was discharged to the atmosphere, resulted in an unexpectedly low incidence of health damage, and it is possible that toxicity to humans is lower than that to animals. Dioxin's notoriety is based primarily on its occurrence as a contaminant in the manufacture of Agent

Orange, a defoliant used in the Vietnam War in the 1960s.⁶⁹ Compensation and pension benefits are being paid to the veterans who were exposed to it and to their dependents.

The mention of dioxins and related compounds such as bromodioxins immediately raises fears. The amounts of dioxins emitted by incinerators are hotly disputed by environmentalists on the one hand and incinerator manufacturers on the other, but plans to construct incinerators anywhere are certain to meet with opposition from the inhabitants and this, allied to the need for the incinerator to be near a town, both for ease of garbage collection and electricity transmission, makes it surprising that even one-eighth of U.S. garbage is disposed of in this way.

Worries about incineration have even led to attacks on cremation, long accepted as the most environmentally acceptable way of disposing of the dead. It now appears that cremation consumes substantial amounts of natural gas and increases the burden of carbon dioxide, sulfur dioxide, and nitrogen oxides in the atmosphere. It converts precious fixed nitrogen into elementary nitrogen. Because of dental fillings, it also produces mercury pollution, and it is now estimated that 10% of the mercury in North Sea fish comes from cremations.

Among the “greener” options is a process called resomation, which has had modest success. In the United States, it is a common way to dispose of bodies donated to medical science, but it is still resisted in Europe. The body is placed in a bag and lowered into a so-called resomator, which is filled with potassium hydroxide solution and heated to 160°C. The result is a greenish, DNA-free liquid and a powdery mass of white bone. There are no emissions and tiny fuel costs.

20.4.5.4 Sanitary Landfill

Landfill remains the fate of 54.2% of municipal solid wastes in the United States. Old data from 1993 showed that U.S. landfills consisted of 40–50% paper waste, 20–30% construction debris, and 1.2% disposable diapers. The number of sites has decreased from 8000 in 1988 to 1900 in 2009 but the capacity has remained more or less constant. Thus new landfills are much larger than old ones. They are also organized on much stricter lines. Even so, the Fresh Kills Landfill on Staten Island has been closed and is being transformed into a park. It was claimed not only to be the world’s largest landfill, but the world’s largest manmade structure. The federal landfill standards are listed in Table 20.7. Landfills still rely on large holes in the ground, but these must be lined to prevent contamination of groundwater and generally regulated in other ways.

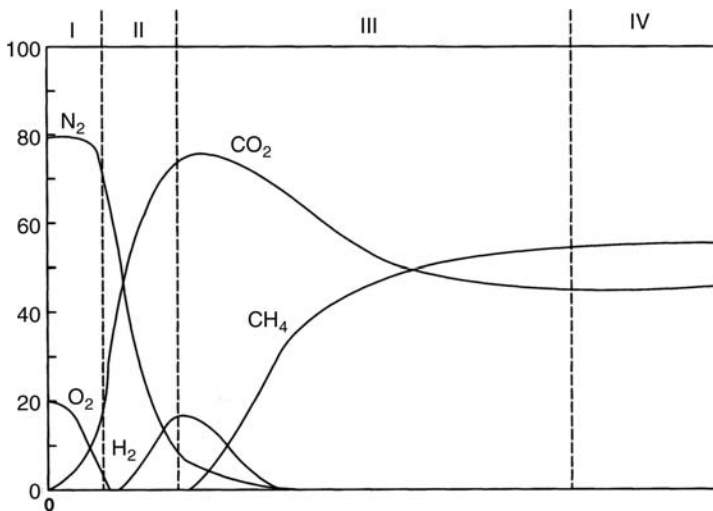
Because biodegradable organic matter is present, landfill sites exude gas. The principal gases are nitrogen, oxygen, carbon dioxide, and methane, but ammonia, carbon monoxide, hydrogen, hydrogen sulfide, and volatile organic compounds are also present in small amounts. The last of these probably arise from household cleaners, hair sprays, and paints. The gases cannot be left to diffuse into the atmosphere. Methane, in particular, is a powerful greenhouse gas. Ammonia and hydrogen sulfide have an unpleasant odor. Methane/oxygen mixtures are liable to explode. Landfill sites are normally capped and mined for their combustible gases, which are sometimes burned to provide electricity.

TABLE 20.7 Federal Landfill Standards

- *Location restrictions* ensure that landfills are built in suitable geological areas away from faults, wetlands, flood plains, or other restricted areas.
- *Linings* are geomembrane or plastic sheets reinforced with 2 feet of clay on the bottom and sides of landfills.
- *Operating practices* such as compacting and covering waste frequently with several inches of soil help reduce odor; control litter, insects, and rodents; and protect public health.
- *Groundwater monitoring* requires testing groundwater wells to determine whether waste materials have escaped from the landfill.
- *Closure and postclosure care* include covering landfills and providing long-term care of closed landfills.
- *Corrective action* controls and cleans up landfill releases and achieves groundwater protection standards.
- *Financial assurance* provides funding for environmental protection during and after landfill closure (i.e., closure and postclosure care).

A landfill site has a life cycle for gas emissions (Fig. 20.13).⁷⁰ In stage I, nitrogen and oxygen are displaced from the landfill as aerobic decomposition starts. In stage II, aerobic decomposition is dominant and produces carbon dioxide. The oxygen is consumed by stage III, and methane production rises as anaerobic digestion takes over. By stage IV, the site has settled down to a steady production of methane, which may be maintained for several years. That is not to say that everything biodegrades. Ten year old hotdogs and newspapers are brought up intact.

The availability of potential landfill sites is decreasing rapidly even in such huge countries as the United States, and the problem is more acute in crowded areas such as northwest Europe. To encourage other forms of waste disposal, there are landfill taxes throughout the European Union and member states must reduce the amount of


FIGURE 20.13 Percentage composition of gases from landfill.

biodegradable municipal waste going to landfill. Based on 1995 levels, the total amount had to be reduced to 75% by 2006, 50% by 2009, and 35% by 2016.⁷¹ This does not seem to have been wholly successful. A 2010 report⁷² states that “The implementation of the Directive on the landfill of waste remains highly unsatisfactory There are still a large number of illegal landfills A vast majority of Member States did not meet the deadline of 16 July 2009 to ensure that all sub-standard landfills (unless specifically derogated) that existed before the introduction of the Directive complied with its requirements. Only nine Member States report having met the 2006 targets for the diversion of biodegradable municipal waste from landfills and capture of landfill gas appears insufficient.”

In the United Kingdom, waste is classified as inactive or active. Concrete, brick, glass, soil, clay, and gravel are classified as inactive together with earth excavated for foundations. Active waste covers all other forms of waste such as wood, ductwork, piping, and plastics.

In 2010 inactive waste was taxed at £2.50 per metric ton; the rate for active waste was £24/metric ton before 2008, and this has increased annually by £8/metric ton. In 2010 it was £40/metric ton and £48/metric ton by 2011.

An increase in incineration facilities, however, is probably not politically practicable, nor necessarily desirable. Recycling and reduction of waste are the only clear solutions and they are more easily recommended than achieved. The adoption of biodegradable plastics would be a contribution to the problem and would at least avoid the unsightliness of plastic bags being blown about the landscape but, if landfilled, the fact that they decomposed would not necessarily be of help. Indeed, there is evidence that plastic bags help stabilize landfill sites and prevent garbage avalanches.

20.4.6 Petrochemical Industry Wastes

The petrochemical industry operates on a huge scale and produces waste organics and catalyst residues together with large quantities of water contaminated with small amounts of hydrocarbons, phenol, and their derivatives.^{73,74} These might be toxic to sewage plant microorganisms, thus bringing the sewage works to a halt. It has proved possible, however, to develop strains of microorganism that can cope. Petrochemical plants thus have highly aerated “bug pits” in which petrochemical-eating “bugs” digest the effluents.

Heavy metals are not normally found in organic chemical plants except as part of a catalyst system. The most toxic metals are cadmium, lead, mercury, beryllium, and arsenic; several others are harmful. If they do occur, every trace of them must be removed and the methods employed are:

1. Precipitation if an insoluble derivative is accessible and does not give colloids.
2. Cation exchange techniques, which are suitable for lead, copper, zinc, mercury, chromium, nickel, and arsenic.
3. Solvent extraction. Nickel ions may be extracted with dinonylnaphthalene-sulfonic acid; zinc and cadmium with di-2-ethylhexylphosphoric acid and

copper with quaternary amines [e.g., Aliquat 336, which is a quaternary ammonium chloride with one methyl group and the other three groups made up of a mixture of C₈ (octyl) and C₁₀ (decyl) chains with C₈ predominating].

Harmful dissolved salts are removed by ion exchange or electrodialysis. Activated carbon and activated silica will adsorb small quantities of toxic organic compounds. Powerful oxidation will render harmless such materials as amines or aldehydes. Chlorination is suitably powerful but leads to the danger of organochlorine compounds that have then to be separated. Electrochemical methods are often used to remove suspensions of oils or paints in a type of froth flotation. Electrolytic hydrogen carries suspended oils upwards so that they can be skimmed off.

Organic chemical wastes usually occur as gases, liquid streams, or sludges and do not present the handling difficulties of municipal solid wastes. Gases are flared at the stack if combustible; if not they may be scrubbed or treated with liquids. Liquids and sludges are usually treated thermally at a high temperature (400–850°C) with or without oxygen. Sophisticated furnaces are required to avoid formation of dioxins and other toxic combustion products. Liquid injection incinerators work for gases and liquids; rotary kilns and fluidized bed incinerators will handle gases, liquids, solids, and sludges. Combustion heat is recovered by raising steam. Pyrolysis technology, in contrast, uses high temperatures in a low-oxygen environment to break down waste products into less complex materials. One advantage associated with this technology is that inorganic constituents are not volatilized; instead, they form an insoluble residue.

Particularly dangerous wastes may be handled in a plasma incineration system where the waste is introduced into an electric arc at above 3000°C, where molecules are completely atomized or ionized and, on cooling, recombine to give small, simple, nontoxic molecules.

20.4.7 Other Environmental Problems

A discussion of the numerous sources and types of pollution in addition to the above is beyond the scope of this book. For example, endocrine disruptors – the mimicking of the female hormone in males – have been widely publicized. Numerous chemicals have been implicated including phthalates, bisphenol A, and nonylphenol ethoxylate. Although it is possible that the phenomenon exists in lower species, it has not been proved in humans. This is not to say that this and other suspected problems are trivial. What it does mean is that the utmost in scientific sophistication and integrity must be applied to their analysis.

20.5 VALEDICTION

We can hardly have a chapter about sustainability without offering some conclusions about the threats to civilization-as-we-know-it, even though, in the immortal words of Yogi Berra, “It’s tough to make predictions, especially about the future.” Potential

disasters include the ozone layer, mass starvation, global warming, emergence of a supervirus, total nuclear war, and many more.⁷⁵

It is clear that no one is going to take the drastic steps required substantially to reduce greenhouse gas emissions. At the worst, the polar icecap will melt, and the earth will become too hot for human beings. The less extreme scenario is that the tropics become too hot for life and there is a mass migration toward the poles, a migration that would be accompanied by wars and random violence, but not necessarily by the extinction of human life. The migration could well result in a nuclear war, which could lead to a “nuclear winter.” As Robert Frost puts it, “Some say the world will end in fire; some say in ice.” There is no evidence that humankind as a whole has the will or the means to do much about these threats, and we must hope the predictions are wrong.

The only current fully operational source of non-carbon dioxide emitting energy is nuclear power. It has been around for half a century, but the disaster at Fukushima in Japan has been a setback. Germany has declared its intentions to close its own reactors by 2022. There needs to be an agreement not to build in seismically active zones. Wind turbines, wave power, and photoelectric power are little beyond the pilot plant stage and, on a full life cycle basis, are economically unattractive. The world is going to depend mainly on fossil fuels for at least a generation.

The food problem is surmountable if the political and cultural difficulties can be solved. Famine occurs because of war not because of climate. Agriculture in the developing world is inefficient, and its people’s enthusiasm for meat-eating counterproductive. The European prejudice against GM crops is absurd as is the U.S. enthusiasm for corn-based biofuels. Science can provide fertilizers, seeds, pesticides, and everything that is needed for a flourishing agriculture even in arid zones, but there is no way of surviving the juggernaut of war.

The earth cannot support nine billion at the level expected by U.S. citizens. As the old Chinese proverb does not say, “If you give a man a fish, you feed him for a day. If you give him a trawler, he will deplete fish stocks.” Birth rate can be reduced with the aid of chemistry (contraceptive pills) and the growth of female emancipation, but not all cultures favor this. The late Yasir Arafat, President of the Palestinian Authority, used to say that “The womb of the Arab woman is my strongest weapon.” In general, the Arab world is anxious to keep its womenfolk in subjection and the birth rate high.

A theme of this book has been the Chinese “economic miracle.” Huge sections of manufacturing industry have migrated to Asia-Pacific. Eighty percent of the world’s toys are made in China.⁷⁶ But the Japanese economic miracle of the 1970s now seems to have run into the sand and it is possible China will do the same. China has an ageing population, a shortage of labor (migratory labor is no longer prepared to work for low wages), and a rising middle class, which is demanding political rights. Pollution levels are terrifying and health and safety legislation largely ignored. The Chinese government has, to its credit, managed to avert the famines brought about by Mao Zedong’s “cultural revolution” and “great leap forward” but how far can this continue? Centralized control always goes hand in hand with corruption, which in turn is economically inefficient.

On the other hand, one should reflect on the relatively short time that North Americans/West Europeans have been dominant. While the Europeans were lost in “the dark ages” and America had only just been “discovered,” the Chinese and Islamic empires were the superpowers, separated from each other, fortunately, by the barely passable Taklamakan Desert. Under the medieval Arab caliphate, and again under the Persian and Turkish dynasties, the empire of Islam was the most powerful, creative, and enlightened region in the world. The Chinese empire too was an advanced civilization responsible, as Joseph Needham has pointed out,⁷⁷ for the invention of almost everything except glass. The Islamic empire declined after the disastrous failure of the second siege of Vienna in 1683. The Chinese empire declined after the death of Ch’ien-lung in 1796. The present Chinese government, significantly, has recently appointed a commission to advise on why China missed out on the Industrial Revolution.

China has managed to hold down wages while selling its products abroad and has hence built up a massive balance of payments surplus. The combination of Western capitalism with political repression has produced an economy that exports capital to developed countries, in contrast to the conventional pattern where the developed world exports capital to the developing world.

The problem of fate of the world is overconstrained. Every problem we can solve is part of a larger problem we cannot solve. The difficulties lie with people, but it is also people who can solve the difficulties. What happens in overconstrained systems is either an Armageddon in which the whole system crumbles, or there is a compromise in which as many of the constraints as possible are satisfied to a limited extent. It is to this last compromise that chemistry can contribute, with the products and the ingenuity described in this book.

ENDNOTES

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APPENDIX A

A Note on Cost Calculations

The accounting side of the chemical industry is perhaps even more complicated than the chemical side. A large chemical company will by law prepare an annual set of accounts (shareholder accounts) on a basis agreed between the company's accountants and its auditors and as defined by legislation, regulation, and best practice. It will also produce a second set of accounts (tax accounts), used to calculate taxes, on a basis laid down by the Internal Revenue Service and legislation. A third set of accounts (management accounts), produced at monthly or weekly intervals, will be for the management, who will use it as a base for their decisions. From the point of view of this book, we are concerned with the items that are taken into account to estimate the cost of manufacture of a particular chemical.

The traditional method of costing a product was to include everything that contributed to its cost. This was called total costing. The items are shown on the left-hand side of Figure A.1. The right-hand side shows the revenue obtained from a sale of the main chemical (ethylene is the example) and possible coproducts (e.g., propylene, butadiene, and butenes).

The total cost is made up of variable costs plus fixed costs. Variable costs are more or less directly proportional to output; fixed costs are independent of output. Raw materials are generally the main variable cost, but one should also add catalyst (which needs regeneration and renewal) and additional chemicals, used perhaps in the separation processes. Variable costs also include utilities – water, electricity, gas from outside sources – and bought-in services. The latter would be negligible in the case of an ethylene cracker but would be larger in cases where more activities were outsourced.

Fixed costs are those more or less independent of output and are made up of overheads, depreciation, interest on loans, and labor (if that is company policy, otherwise they would be variable costs – see below). Overheads are costs that cannot be attached to any specific cost center and are distributed between the various cost centers in a company on a predetermined basis. Overhead costs include head office costs, security personnel, research and development costs, plant maintenance, property taxes, insurance, lease rentals, sales programs, and certain other

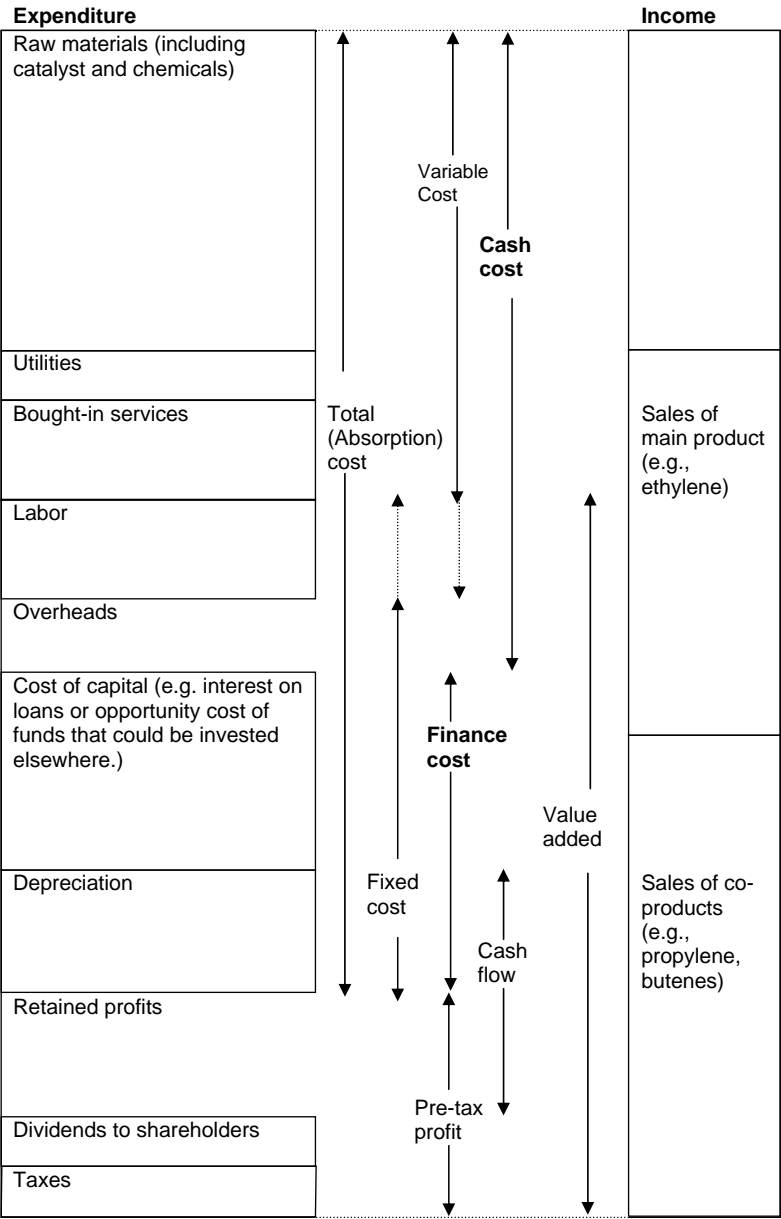


FIGURE A.1 Terms used in cost calculations.

administrative expenses. (In the United Kingdom, the basis of rates is the rateable value of the property, not of the land. It is a property tax, not a land tax.)

None of these overhead costs are part of the direct production cost of the chemical being considered, but under total costing such costs have to be recovered for the company to be profitable. Fixed costs are further subdivided under three headings. Direct fixed costs are made up of operating costs from labor, maintenance, and direct overhead charges. Allocated fixed costs include general plant overhead, insurance, and property taxes. These costs are mostly site-related. If an environmental levy were charged, it would come under this heading.

Finance costs include interest on loans and depreciation. Depreciation is an annual noncash accounting cost to recover the capital cost of the investment. In the nineteenth century, this money was put in a separate account called a sinking fund and could be used to rebuild a plant when it wore out. Today, there is no separate depreciation reserve – instead, the annual depreciation charge reduces the company's profits to reflect the ageing of the plant. The rate at which assets are depreciated is at the discretion of the company's accountants and auditors and will usually differ from the rules laid down by the Internal Revenue Service, which will base taxation on legislation and the tax accounts. If the company has borrowed money to finance its plant, interest on loans will be a fixed cost. This is called the finance cost and is included within the shareholder accounts and the tax accounts. If the company had used surplus funds to finance the plant, the management accounts may include an opportunity cost of capital, but only if it were the policy of the company. Opportunity cost is defined as the rate of return that could have been earned had the surplus funds been otherwise invested.

In-between the fixed and variable costs in Figure A.1, we have inserted the cost of labor. There has been much debate as to whether labor should count as a fixed or variable cost. In the nineteenth century, the foreman at a chemical plant could open the gates at 6 a.m. and sign on the exact amount of casual labor that he needed for the day. Labor was thus related to the output required and was truly a variable cost. In the chemical industry today, workers are generally highly trained and cannot be recruited or dismissed on a daily basis. Furthermore, a plant operating at 50% capacity requires exactly the same number of operatives as when it works at 100% capacity. Hence a modern trend in the chemical industry is to treat labor as a fixed cost that is independent of output. To avoid ambiguity, the term cash cost includes raw materials, utilities, bought-in services, labor, and overheads, that is, a combination of fixed and variable costs.

The revenue received from the sale of the chemicals minus the total cost and other noncash charges is the pretax profit, some of which is owed to the Internal Revenue Service as taxes. Some is distributed to the shareholders and some is retained to finance the company's expansion.

The cash flow has traditionally been defined as the combination of profits and depreciation. More definitively, it may be described as the surplus of cash received over cash paid from operations plus the net cash received from activities including financing (i.e., cash received from taking on loans and the issue of new shares) and investing (such as the acquisition of fixed assets or of a company). Value added is the

amount added to the inputs by the company's efforts; hence it is the sales revenue minus raw materials, utilities, and bought-in services.

Under total costing, the total costs must be recovered by the revenue. However, the use of total costing as a basis for decision making and pricing decisions has been criticized in that, for example, allocation of overheads is arbitrary, and past investments are "sunk" costs. For example, once the plant is built, there is no way one can recover the cost of building it, and as such should be ignored for decision making purposes. In addition, allocation of overheads is a zero sum game; that is, the net profit will be the same however they are allocated within a company's profit and loss account. The "sunk cost" approach is satisfactory if business improves each year. If it does not, depreciation accounting is the better part of valor.

In respect to pricing decisions, the loading of research costs for future products onto current products can be misleading. For example, many pharmaceutical companies claim that it costs them more to manufacture acetaminophen than it costs a generics company, because the research costs for the development of future products need to be included, even though these research costs are not part of the production cost of acetaminophen.

Hence short-term management decisions tend to be based on cash costs. Cash costs are made up of variable costs (including any by-product credits), both direct and allocated fixed costs. Cash costs are crucial. Suppose prices are dropping. If revenue drops below the *total cost*, in the short term the optimal decision may be to continue production as long as revenue is in excess of the variable costs. Technically, one is making a loss, but one would make a larger loss if one ceased production, because any excess of revenue over the variable costs contributes to fixed costs, which have to be paid anyway. If the price drops below the variable cost, then it is sensible to cease production. In the long term, if the price falls below total cost, the optimal decision would be to cease production.

In the long run, all costs become variable costs. Employees can retire or be made redundant. A plant wears out and does not need to be replaced. The total cost of the reinvestment option then needs to be considered. Once the money has been spent, however, the finance costs again become sunk costs and decisions are taken on the basis of variable and fixed costs.

The traditional measure of profitability has been the return on investment (ROI). To calculate this, it is necessary to know the amount of money the investor has put into the project. The return on investment is given by

$$\text{ROI} = \frac{(\text{Gain from Investment} - \text{Cost of Investment})}{\text{Cost of Investment}}$$

In place of Return on Investment or along with it, EBIT and EBITDA are now used as a measure of profitability. They stand for Earnings Before Interest and Taxes, and Earnings Before Interest, Taxes, Depreciation, and Amortization. Two items we have not already mentioned are amortization, which is the progressive reduction in value of nontangible assets, such as the reduction in value of a patent as it nears expiry, and nonoperating income, which is income not related to the typical activities of the

business or organization. Neither of them really concerns us here, but they appear in the standard equations.

$\text{EBIT} = \text{Revenue} - \text{Operating Expenses} + \text{Nonoperating Income}$. This is the revenue minus the sum of the cash cost and any selling, general or administrative expenses, if they haven't already been included, and depreciation and amortization. EBITDA further excludes depreciation and amortization from the calculation and is the revenue minus the sum of the cash cost and any selling, general or administrative expenses.

APPENDIX B

Units and Conversion Factors

Weight

Thousand pounds	Tonnes (metric tons or thousand kg)	Long tons	Short tons
1	0.4536	0.4464	0.5000
2.2046	1	0.9842	1.1023
2.2400	1.0160	1	1.1200
2.0000	0.9072	0.8929	1

Volume

Liters (10^{-3}m^3)	Cubic feet	U.S. gallons	Imperial gallons
1	0.03532	0.2642	0.2200
28.32	1	7.481	6.229
3.785	0.1337	1	0.8327
4.546	0.1605	1.201	1

Pressure

Atmospheres	bar	torr (mm Hg)	psi	kg/cm ²
1	1.01325	760	14.696	1.033
0.9869	1	750.06	14.504	1.020
0.001316	0.001333	1	0.01934	0.00136
0.06805	0.06895	51.715	1	0.0703
0.968	0.980	735.3	14.225	1
(1 bar = 10^5 pascal or N/m ²)				

Industrial Organic Chemicals, Third Edition. By Harold A. Wittcoff, Bryan G. Reuben, and Jeffrey S. Plotkin.

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$$0\text{ K} = -273.15^{\circ}\text{C} = -459.7^{\circ}\text{F}$$

Heat

kJ	kcal	Btu (10^{-5} therms)
1	0.239	0.948
4.184	1	3.968
1.054	0.252	1

One tonne of oil is equivalent to	3.97×10^7 Btu 0.01 teracalories 0.042 terajoules 1.5 tonnes of coal (typical calorific value) 3 tonnes of lignite (typical calorific value) 0.805 tonnes of LNG 1111 m ³ of natural gas 39,200 cubic feet of natural gas 12,000 kWh of electricity
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One kWh = 3412 Btu = 860 kcal

The *BP Statistical Review of World Energy 2011* (from which many of the figures in this appendix are drawn) indicates that “One million metric tonnes of oil produces about 4400 gigawatt-hours of electricity in a modern power station.” This interesting number implies that a modern power station is 36.7% efficient, close to what one would expect on thermodynamic grounds.

Noble Metals

1 lb avoirdupois = 14.58 oz troy. 1000 oz troy = 31.15 kg = 0.03115 tonne.

APPENDIX C

Special Units in the Chemical Industry

PETROLEUM AND REFINERY PRODUCTS

Crude oil and some refinery products are traded in barrels (bbl) of 42 U.S. gallons (gal) (= 35 Imperial gallons). There are claims that bbl stands for blue barrels because oil barrels used to be colored blue by Standard Oil in its early days to distinguish them from food barrels. This is probably incorrect because there are citations for the symbol at least as early as the late 1700s, long before Standard Oil was founded. More likely, the “b” was doubled originally to indicate the plural (1 bl, 2 bbl), or possibly to eliminate any confusion with bl as a symbol for the bale.

As the gallon is a unit of volume, the weight of a barrel depends on the density of the product. Approximate conversion factors follow:

1 metric ton (tonne) = 7.33 bbl crude oil, 8.45 bbl gasoline, 7.80 bbl kerosene, 7.50 bbl gas oil, and 6.70 bbl fuel oil.

1000 pounds (pounds) = 3.32 bbl crude oil, 3.83 bbl gasoline, 3.54 bbl kerosene, 3.40 bbl gas oil, and 3.04 bbl fuel oil.

1 bbl per day \approx 49.8 metric tons/year.

Liquefied petroleum gases are sold by the U.S. gallon or by the metric ton. One metric ton contains 521 gallons of propane, 453 gallons of *n*-butane, or 469 gallons of isobutane. LPG can be mainly propane, mainly butane, or a “mixed” cargo, in which case intermediate conversion factors based on composition must be applied.

GASES

Natural gas is measured in standard cubic feet (scf) at 1 atmosphere (atm) and 60°F or in cubic meters (m^3) at 1 atm and 0°C. $1 \text{ m}^3 = 37.33 \text{ scf}$; $1 \text{ scf} = 0.0268 \text{ m}^3$.

Thermal units (heat liberated when a volume of gas is burned) are sometimes used. Calorific values depend on the composition of the gas but are usually 900–1000 Btu scf^{-1} . Accordingly, 1 therm = 10^5 Btu = 100–110 scf.

Other gases are also measured in scf and m^3 . If the molecular weight of a gas is M , then 10^6 scf of the gas weighs 2.635 M thousand pounds or 1.2 metric tons. For example, 10^6 scf of hydrogen weighs 5.312 thousand pounds (2.4 metric tons) and of oxygen 84.32 thousand pounds. Similarly, 1000 m^3 of a gas weighs 0.0446 M metric tons. Thus 1000 m^3 of hydrogen weighs 0.900 metric ton and 1000 m^3 of oxygen 1.427 metric tons.

COAL TAR PRODUCTS

Coal tar and materials traditionally derived from it such as benzene, toluene, and xylenes are sometimes measured in thousands of U.S. gallons. One thousand U.S. gallons of benzene at 20°C weighs 7320 pounds (3.32 metric tons), of toluene 7210 pounds (3.27 metric tons), of *o*-xylene 7300 pounds (3.31 metric tons), of *m*-xylene 7161 pounds (3.248 metric tons), and of *p*-xylene 7134 pounds (3.236 metric tons).

ETHANOL

Ethanol is measured in mixed volume and concentration units. One Imperial gallon (1.201 U.S. gallons) of 100% ethanol contains the same amount of ethanol as 1.75 proof gallons, and concentration is measured in degrees proof. The specific gravity of ethanol is 0.79; hence 1 proof gallon contains 4.5 pounds (2.04 kg) ethanol. It is also the alcoholic equivalent of a U.S. liquid gallon at 15°C containing 50% ethanol by volume. The metric units are hectoliters (= 100 liters), and concentration is expressed in degrees Gay-Lussac. Ninety-five degrees Gay-Lussac represents 95% by volume at 15°C. One hectoliter = 22 Imperial gallons = 26.4 U.S. gallons. One hectoliter of 100% ethanol weighs 174 pounds (79 kg). The U.S. liquid gallon (as above) is identical with the Queen Anne wine gallon. A U.S. tax gallon for spirits of 100 proof or over is equivalent to the proof gallon; for spirits of less than 100 proof, to the wine gallon.

BIOFUELS

1 metric ton ethanol = 0.57 metric ton oil; 1 bbl ethanol = 0.57 bbl oil.

1 metric ton biodiesel = 0.88 metric ton oil; 1 bbl biodiesel = 0.88 bbl oil.

APPENDIX D

The Importance of Shale Gas and Shale Oil

From the end of World War II to the closing years of the twentieth century the United States was a dominant factor in the world's chemical business, predominantly because of cheap and plentiful gas and oil. Ethylene and some propylene came from the steam cracking of ethane and propane from gas. More propylene came from the catalytic cracking of various fractions for gasoline. As U.S. reserves of natural gas and petroleum waned shale came to the fore.

Shale is a sedimentary rock with laminated layers of clay-like particles. It was known for many years that shale could contain huge amounts of gas and oil. But it held these stubbornly and took its place with the tar sands in Canada as a source of gas and oil from which extraction was difficult. Both have yielded recently, but shale is far in the lead. Necessity fostered progress even as this book was being written. Because insufficient data were available while we were writing the book and because of the importance shale has assumed, we felt it important to describe it in an appendix.

SHALE GAS

Enthusiasts declare that the United States will become the Saudi Arabia of natural gas. In Saudi ample reserves of petroleum were distilled to give fractions that could be cracked predominantly into ethylene with smaller amounts of propylene, C₄ and higher olefin. Shale gas is already about 90 percent ethylene. Thus cracking may not provide sufficient quantities of propylene. The answer is previously devised creative chemistry in which propane is dehydrogenated to propylene or in which ethylene is dimerized to C₄ olefins and the dimers metathesized with more ethylene to give propylene (Section 4.14). This could solve a possible propylene shortage.

It is difficult to export gas. But it is equally hard to import it, and many countries will be faced with this problem. A gas-importing terminal was built in the United States before shale gas declared its potential. Now that terminal and eleven others are being converted to gas export terminals. This is further evidence that the United States anticipates a dominant position, including export, in the shale gas business.

Each shale-containing area is called a basin. There are seven active areas in operation in the United States in 2013, although 26 possibilities have been located. Each of these is referred to as a shale and they are located in the East, Midwest, South, and West of the country. What do they? They offer up their oil and their gas to an energy hungry world.

Shale gas recovery was made possible because of horizontal drilling and hydraulic fracturing or fracking. Shale deposits lie much deeper in the ground than natural gas deposits. Thus conventional vertical drilling is required to reach them. Then the drilling must become horizontal through the deposit of shale to provide areas for the fracking, which in turn provides fissures and cracks through which the oil can flow. To facilitate the actual fracking a mixture of sand and water is injected together with two to three percent of chemicals. The combination of sand, water, and chemicals is known as fracturing fluid. The purpose of the chemicals is to facilitate by surface activity, or other phenomenon, the entry of the fracking mixture into the shale. As might be expected there are numerous state and federal statutes that regulate these procedures.

The sand is silica as might be expected. It is called a proppant because it props up fractures in the shale. Each installation requires about three million gallons of water. This is roughly the same as required for other industrial activities such as electric power generation, agriculture, or use in municipalities. It is used well below the drinking water ground level and thus will not in ordinary circumstances affect potable water. After fracking the water may simply reside where it is. In some instances it must be recovered. It may be recycled if necessary, reused for hydraulic fracture, or simply treated and discharged.

An important advantage of fracking is that it provides greater exposure to the formation creating as many as six wells from one operation rather than the one that results from vertical drilling. This makes the collection of the gas and its distribution more complex, although the product is produced more handily. Also, six to seven acres are required for the six wells as described above. Considerably more is required for a similar number of traditional wells.

Much has been said about the century's supply of gas that exists in the United States. In fact, if shale gas is added to the current decreasing supply of natural gas there is, at the present rate of consumption in 2012, a 116 year of supply. Gas-driven automobiles and gasoline prepared from gas are two strong possibilities for consumption of gas as is electricity from gas rather than from coal.

Some shale emits radioactivity, and there is legislation that relates to this as there is to other areas such as impact on land, protection of rare animal species and plants, hazardous waste clean up, and safety and health in the work place. Quantities of emissions such as NO_x , SO_2 , H_2S , CH_4 , and particulates, are carefully regulated. A long list of possible additives include biocides, oxygen scavengers, corrosion

inhibitors, and various acids. These are dispersed in the sand and the three million gallons of water required. Air emissions accompany the operation and include, among many other compounds, H_2S and NO_2 . These are no greater than the emissions from a coal gas operation and are again carefully regulated.

SHALE OIL

In the United States considerably more effort has been devoted to shale gas than to shale oil development. In part this is because the oil is more difficult to handle, and to convert it so that it resembles petroleum. It requires additional steps above ground where it must be heated in a retort after which it is pyrolyzed at 650–700 °F. It is because of this treatment that shale becomes a liquid resembling petroleum. All of the problems described earlier for shale gas isolation and use are encountered with shale oil. But it nonetheless is being developed throughout the world because it provides a solution to the problem presented by diminishing supplies of petroleum.

- Acetaldehyde, 165–167, 187
 - aldol condensation with, 187
- Acetic acid, 442
- Acetic (ethanoic) acid, 439
- Acetic anhydride, 442
- Acetone, 233
 - alternative route, 234
 - cumene/phenol process as major source of, 233
 - major chemical, use for, 235
 - oxidative dehydrogenation, 234
 - Shell process, 234
 - Wacker process, 234
- Acetophenone, 179, 233, 245
 - converted to styrene, 245
- Acetoxylation, 421
 - of 1,4-butanediol, 294
 - of propylene, 247
- N*-Acetyl-*p*-aminophenol, 444
- Acetylene, 417, 418
 - carbonylation of, 424
 - production of, 488, 683
- Acidic zeolite catalysts
 - alkane cracking, mechanism of, 652
- Acrolein, 268–269
 - glutaraldehyde manufactured in small quantities from, 269
 - mechanism of formation, 224
 - Meerwein–Ponndorf reduction, 266
- Acrylamide, 227, 231, 266–267
 - Nitto, microbiological conversion of acrylonitrile, 267
 - production, 267
 - uses, 267
- Acrylic acid, 222
 - biorenewable processes to, 225–226
 - markets, 226–227
 - production methods, 223
- Acrylonitrile, 227–230
 - graft polymerization of, 270
 - mechanism of formation, 229
 - Michael condensation of, 613
 - uses of, 230–231
- Acrylonitrile–butadiene–styrene (ABS)
 - resins, 280, 283, 284
- Acrylonitrile derivatives, 270
- Adhesives, 17, 37, 151, 169, 226, 259, 319, 334, 435, 535, 562, 583, 592, 630, 631, 707
- Adipic acid, 206, 285, 289, 294, 344–349
 - available from petrochemical sources, 507
 - condens with hexamethylenediamine, 344
 - nylons from, 349
 - production, 330, 331, 684
- Adiponitrile, 285–289, 288, 350
 - DuPont synthesis of, 658
- Air oxidation, 479
- Air pollution, 4, 226, 490, 491, 736, 744, 745, 747
 - chemical nature of, 744
 - combustion processes, 745
- Aldol condensation, 166, 187, 188, 189, 241, 255, 258, 389, 692
- Aliphatic isocyanates, 684
- Alkanes, 463
 - carbon black, 472–473
 - C2–C4 alkanes, functionalization of aromatization of, 471–472
 - dehydrogenation of, 470–471

Alkanes (*Continued*)

- oxidation of, 468–470
- functionalization of, 464
- methane, functionalization of, 464
 - aromatization of, 467
 - dimerization of, 466–467
 - methane to methanol/
 - formaldehyde, 464–466
 - natural gas and petroleum, 463
- Alkyd paints, 392, 393
- Alkyd resins, 391, 392
- Alkylation reaction, 105, 115, 116, 124–125, 128, 134, 221, 482
 - of benzene with propylene, 231
 - with *n*-butenes and isobutene, 115
 - Exelus's alkylation of toluene, 377
 - Friedel–Crafts alkylation, 362, 689
 - of isobutane, 651
 - at lower temperatures and pressures, 231
 - of phenol with nonanol, 298
 - toluene with propylene, 653
- Alkylbenzenes, 361–362
 - from alkylate benzene, 470
 - with C₁₀–C₁₄ side chains, 361
 - linear, 509, 652
 - properties, 361
 - sulfonates, 361, 460, 519
- Alkylbenzene sulfonate, 361, 460, 519
- Alkylphenols, 171, 342, 353
- Alkyl polyglycosides, 519
- Allyl alcohol for synthesis of
 - 1,4-butanediol, 265
- Allyl chloride, 263
 - converted by ammonia to mono-, di-, and triallylamines, 265
 - and epichlorohydrin, 263–265
 - from propylene, 380
- Allylic hydrogens, 594
- Aluminophosphates, 116, 667
- Alzheimer's disease, 132, 499
- American Cyanamid, 59, 418
- American National Standard Institute (ANSI), 87
- Amino-containing resin, 506
- Aminoethyl alcohols, 142, 171, 198
- Ammonia
 - allyl chloride is converted by, 265
 - anhydrous, 485
 - bisulfate decomposes to, 238

- catalytic oxidation of, 331
- convert fatty acid to nitrile through
 - successive dehydrations, 502
- to depress formation of a triamine, 285
- direct amination of benzene with, 355
- ethylene dichloride with, 200
- ethylene oxide reacts with, 171
- Haber process for, 674
- interaction of carbon monoxide and, 409
- interaction of ethylene oxide with, 198
- intermolecular amination of toluene
 - with, 379
- and its derivatives, 430–435
- oxidized to, 433
- n*-propanol react with, 185
- reaction with acetaldehyde, 190
- recovered and recycled as a feedstock, 240
- synthesis of caprolactam, 353
- world ammonia capacity, 425
- Ammonia-based hydroxylamine, 434
- Ammonium (cyanate), 432
- Ammoxidation, 40, 212, 222, 227, 228, 239, 288, 299, 375, 395, 400, 408, 409, 411, 434, 463, 469
 - to hydrocyanic acid, 408
 - of propylene, 674
 - route to acrylonitrile, 212
- Amorphous graphite, 472
- Andrussow reaction, between methane, air, and ammonia, 408
- Aniline, 233, 292, 354–356, 619
 - capital cost of process, 355
 - 4,4'-diphenylmethane isocyanate, 357
 - Asahi process, 358
 - Catalytica Associates, 358
 - clever process, 358
 - diisocyanates, uses, 360
 - Hüls process, 359
 - MDI end-use profile, 360
 - noncellular applications, 360
 - nonyellowing isocyanates, 360
 - selected "aliphatic" diisocyanates., 361
 - uncommercialized nonphosgene
 - routes, 359
 - involve ammonolysis of phenol, 355
 - major uses, 356
 - from phenol, 344
 - production, 354
 - by DuPont, 355

- Antarctic ozone layer, 740
- Anthracene, 371, 478, 479, 480
- Anthraquinone, 370–371, 394
 - hydrogen peroxide, 371–372
- Antibodies, catalytic, 663
- Antibody-catalyzed reactions, 663, 664
- Antimony–uranium oxide catalyst, 674
- Aqueous phase reforming (APR), 557
- Archer Daniels Midland (ADM), 516
- Arco
 - manufacturer of propylene oxide from which polyols, 62
 - to obtain conversions to C₂–C₇ compounds, 466
 - route to allyl alcohol for synthesis of 1,4-butanediol, 266
 - two-for-one process for manufacture of propylene oxide and *t*-butanol, 42
- Aromatic feedstocks, 452
- Aromatics, primary production of, 324
- Aromatization, 120, 189, 464
 - aromatics yield, 471
 - butene, 668
 - of C₂–C₄ alkanes, 471
 - of methane, 467
- Asbestos exposure, 33
- Asia
 - coal accounts for, 717
 - cost of diesel fuel, 133
 - cracker feedstocks, 103
 - for hydrocrackers, 211
 - production of chemicals, 50
- Asphalt emulsifier, 506
- Atactic polymers, 595
- Aurabon process, developed by UOP, 126
- Automobile batteries, 754
- Automobile emissions, 346, 641
 - control, 649
- Automobile tire, 280
 - components, 280
 - of heavy duty truck, 281
 - natural rubber, content, 281
 - neodymium polybutadiene, 281
 - premium tires, 281
 - requirement for, 281
 - rubber/SBR blend, 281
- Bacampicillin, 669
- Badische Anilin und Soda Fabrik (BASF), 430
- BASF, 53, 422, 688
 - cracker, 114, 129
 - ethylene capacity, 53
 - methanol prepared by, 435
 - pioneered biocatalyst production of riboflavin and, 697
 - process starting with butadiene, 684
 - R&D spending, 37
 - as top chemical companies 1970–2009, 56
 - two-for-one electrochemical process to produce chemicals, 691
- Bayer
 - coal requirement for synthesis of organic chemicals, 490
 - compelled to demerge into operating subsidiaries, 62
 - ethylene cracker, 54
 - polyether polyols business to, 62
 - R&D spending, 37
 - as top chemical companies, 38, 56
 - to use nitric oxide as redox reagent in synthesis of dimethyl carbonate, 336
- Beckmann rearrangement, 350, 352, 353
- Benzene
 - based cyclohexane, 683
 - carcinogenicity, fears of, 32
 - from coke oven distillate, 323
 - cyclohexane dehydrogenated to, 330
 - Friedel-Crafts alkylation, 362
 - global benzene demand, 326
 - major uses for, 326
 - oxidation of, 684
 - reaction with ethylene, 326
 - sources, 323
 - in United States as chemical feedstock, 323
 - world benzene trade, 325
- 1,3,5-Benzenetricarboxylic acid
 - second generation hyperbranched polymer, 616
- Benzoic acid, 222, 328, 353, 380, 381, 386, 743
 - to phenol, conversion, 329
- Benzoylglucuronic acid, 743
- Benzyl chloride, 376, 380, 381, 457, 458

- Bergius process, 485
 Bhopal disaster, 450
 Bimetallic ruthenium/cobalt system, 441
 Bimodal HDPE, 149
 Bimodal resins, 149
 Biodegradable films, properties of, 700
 Biodegradable polymers
 polylactate, 552
 production of, 699
 Biodiesel, 513, 516
 manufacture, 512
 purification, 265
 Biogasoline, 557
 Biopol, 702
 Biopolymer production capacity, 700
 Biphasic Acid Scavenging utilizing Ionic Liquids (BASIL) process, 688
 Bisimine ligands, 603
 Bismuth phosphomolybdate, 674
 Bisphenol A (BPA), 234, 261, 262, 265, 333, 681
 by-products, 333
 condensates with epichlorohydrin, 611
 environmental problems, 340, 341
 lesser volume uses for, 337
 NEXARTM polymers, 338
 polyarylates, 338
 poly(ether imides), 338
 polyimide, 340
 polysulfone, 338
 tetrabromobisphenol A, 340
 polycarbonate grade, 333
 production of, 333, 653
 sodium salt, 612
 Bitumen, 137
 Biuret trimer, 611
 Bleaching process, 498
 Block copolymers, 590, 591
 styrene-butadiene-styrene, 591, 592
 Blow extrusion, 633
 β -methylthiopropionaldehyde, 268
 reaction with hydrocyanic acid, 268
 Boots process, 692
 Bosch's solution, 430
 Bouveault-Blanc reaction, 508
 BPA. *See* Bisphenol A (BPA)
BP Statistical Review of World Energy
 2011, 772
 Branched polymers (BP)
- Bristol-Myers Squibb, 696
 British coal industry, 490
 British Gas process, 487
 Bromine, 205
 Chinese venture into bromine
 production, 741
 promoter, 398, 649
 replacement of, 511
 Bromodioxins, 756
 Bromomethane (methyl bromide), 416
 Brønsted acids, 651, 652
 Butadiene, 273
 by acetoxylation, 421
 BASF developed benign process, 684
 butadiene-free raffinate, 275
 to caprolactam route, 289
 chemicals and polymers from, 277
 chlorination of, 287
 demand pattern, 277
 DuPont synthesis of adiponitrile
 from, 658
 lesser volume chemicals from, 289
 adipic acid, 294
 butadiene monoepoxide, 296
 1,4-butanediol, 294
 cyclization, 289–290
 Diels–Alder reactions, 293–294
 dimerization, 291–292
 dimethyl-2,6-naphthalene
 dicarboxylate, 295, 296
 trans-1,4-hexadiene, 295
 trimerization, 291–292
 process for dimerizing, 283
 styrene-butadiene-styrene block
 copolymer, 592
 telomerization of, 483
 trimerizes over a titanium
 tetrachloride-dialkylaluminum
 chloride, 291
 Butadiene–nickel–ligand–ethylene
 complex, 658
 1,3-butadiene, removal of, 274
 Butane
 aromatics yield from aromatization, 471
 based maleic anhydride processes, 304
 dehydrogenation of, 470
 monoepoxide, 296
 oxidation plants, 441
 use in gasoline for volatility, 97

- n*-Butane
 - to 1,4-butanediol and tetrahydrofuran, 469, 470
 - catalytic oxidation of, 167, 469
 - dehydrogenated to butadiene, 274, 463
 - isomerization, 128
 - and light naphtha, 303
 - to maleic anhydride, 400
- 1,4-Butanediol, 294, 348, 419, 420, 421, 423, 469, 553
 - manufacture, 40
- Butane monoepoxide, 296
- n*-Butane/naphtha, oxidation of, 463
- 2-Butanol, 302
- 2-Butanone, 302
- Butenes, 3, 93, 94, 122, 154, 221, 275, 285, 298, 302, 303, 362, 675, 766
 - 1- and 2-butenes
 - chemicals and polymers from, 302, 303
 - oxidation of, 304
 - dehydrogenation, 274
 - fuel and chemical uses, 274
- Butylated hydroxytoluene (BHT), 299
- tert*-Butylbenzaldehyde (TBA), 691
 - electrosynthesis of, 691
- 1-Butyl-3-methylimidazolium chloride, 690
- γ -Butyrolactone, 420

- Caffeine, 686
- Calcium carbide, 418
- Calcium hydroxide, 683
- Capital intensity
 - and corollaries, 23
 - and economies of scale, 22
- Caprolactam, 46, 289, 341, 344, 347, 349–354, 381, 548
 - ionic polymerization of, 565, 567
 - routes to, 350–351
 - Toray process to, 690
- Carbazole, 479, 480
 - from air-oxidation of diphenylamine, 619
- Carbide
 - process, 418
 - use of, 488
- Carbohydrate gums. *See* Carbohydrates
- Carbohydrates, 523
 - cellulose, 535–539
 - fermentation/biotechnology, 544
 - amino acids, 547
- L-aspartic acid, 548–549
- biofuels, 554
- biomass, as feedstock, 556
- biotechnology vs. synthesis gas, 557
- Brazilian experience, 554–555
- catalytic bioforming, 556–557
- L-cysteine, 549
- fermentation/renewables
 - scenarios, 551–553
- L-glutamic acid, 547
- L-lysine, 547–548
- polymers, 550
- protein by recombinant DNA
 - technology, 550–551
- U.S. bioethanol, renewable energy
 - source, 555–556
- furfural, 530–532
- gums, 543–544
- isosorbide, 530
- sorbitol, 523–530
- source of organic chemicals, 97
- starch, 532–535
- sugars, 523–530
- wood, miscellaneous chemicals from, 539
 - Levulinic acid, 542–543
 - natural vanillin, 541–542
- Carbon black, 472–473
 - global market, 473
 - silica, combination, 473
 - world consumption of, 472
- Carbon dioxide, 685, 725, 755
 - absorbing systems, 725
 - atmospheric levels of, 709
- Carbon disulfide, 416
 - replacement of, 689
- Carbon monoxide, 657
 - based routes, 456, 457
 - oxidation of, 671, 672
 - yields phosgene, 454
- Carbonylation, 452
 - of acetylene, 367
 - of ethylene, 186
 - methanol, 167, 440, 441, 455
 - phase transfer carbonylation of benzyl chloride, 457
 - propylene, 239
 - of toluene, 381
- Carbonyl sulfide (COS), 428
- Cargill Dow process, 702

- Carnot efficiency, 729
- Castor oil, 510
- nylon 11, 511
- Catalysis, 637
- by acids and bases, 651–654
 - catalyst markets, 647–650
 - catalyst selection, 637
 - catalyst deactivation, 642
 - nonequilibrium products,
 - access, 642–643
 - reaction velocity and
 - selectivity, 638–641
 - unchanged catalyst, recovery of, 641
 - coordination catalysis, 657
 - asymmetric synthesis, 660–661
 - catalysts for stereoregular
 - compounds, 658–660
 - dual function catalysis, 654–655
 - enzymes, 661
 - catalytic antibodies, 663–664
 - future
 - catalyst design, 673
 - catalyst discovery *via* high throughput
 - experimentation, 676–677
 - catalysts with greater activity, 674–675
 - higher selectivities, 673–674
 - mimic natural catalysts, 676
 - new reactions, 675
 - pollution problems, 675
 - homogeneous/heterogeneous
 - catalysis, 643
 - heterogeneous catalysts,
 - reactors, 644–646
 - homogeneous catalysts,
 - immobilization, 646
 - by metals, semiconductors, and
 - insulators, 655–656
 - automobile emission control, 656–657
 - nanocatalysis, 670–673
 - phase-transfer/fluorous biphasic, 669–670
 - platinum group metals, 650
 - shape-selective catalysts, 664–669
 - sulfuric acid, 651
- Catalysts
- henium–alumina, 105
 - heterogeneous, 646, 655
 - homogeneous, 643
 - metallocene, 40, 149, 600, 649
 - nickel, 129
 - phosphole, 603
 - platinum, 734
 - platinum–palladium–rhodium, 675
 - polyolefin, 603
 - rhodium, 257
 - selective, 675
 - smectite, 669
 - titanium, 249
 - zeolite, 215, 231, 452
 - Ziegler–Natta catalysts, 149, 569, 595,
 - 604, 658
- Catalytic antibodies, 663
- Catalytic cracking, 114, 651
- fluidized bed catalytic cracking of gas oil
 - product mix, 116
 - to give C₃ and C₄ olefins, 133
 - impetus from World War II, 115
 - improved catalysts for, 116
 - lead to formation of branched chain
 - compounds, 115
 - mechanism of, 117–119
 - in mid-1960s, 115
 - petroleum refining, 653
 - propylene production, 115
- Catalytic reactions, summary, 638
- Catalytic reforming, 119–122, 654
- C₉+ aromatics fraction, 121
 - C₈ fraction, 121, 122
 - hydrogen and the C₁–C₄ alkanes, as
 - product, 121
 - production ratio vs. U.S. chemicals
 - demand, 121
 - provide toluene and xylenes for unleaded
 - gasoline, 121
 - typical reformer aromatic yields, 120
- Catalytic Rich Gas (CRG) process, 485
- Catalyzed reactions, reactors for, 645
- Catechol, 364
- from benzene, 370
 - from caustic hydrolysis of
 - ortho*-chlorophenol, 369
 - and hydroquinone, 366, 370
 - methylation of, 541
- Cationic photoinitiators, 583
- Cationic polymerization, 588
- Cativa process, 440
- C₄-based chemicals, 273
- composition, 275
- C₁ chemistry, 97

- Celanese acid optimization (AO)
 - process, 440
- Celanese process, 507
- Cell enzymes, 701
- Cellulose, 94, 171, 186, 269, 444, 536
 - cellulose xanthate, 538
 - derivatives, 536
 - to 5-ethoxymethyl furfural, 532
 - hydrolyzed with acid, 557
 - nitrocellulose, 538
 - as such for papermaking, 540
 - triacetate, 537
- Cellulose acetate, 230, 389, 444, 537, 563, 564
- Cellulose/hemicellulose, 557
- Cellulose nitrate, 389, 433
- Cellulosic ethanol
 - EROEI of, 557
- C₁₈ fatty acid, 501
- C₂₂ fatty acid, 496
- Chain growth polymerization, 572
- Chain termination, 587
- Chain transfer, 576
- Chemical industry
 - acquisitions, 56
 - bibliography, 6
 - biofuels, 774
 - books, 7–8
 - characteristics of, 22–24
 - chemical arms of petroleum companies, 59
 - coal tar products, 773
 - consumers, 25
 - criticality, 24–26
 - disasters, 31
 - dislocation, 41–43
 - economic cycles, 55, 56
 - economies of scale, 22–24
 - employment of, 35
 - encyclopedias, 6–7
 - ethanol, 774
 - European Union GDP, 16
 - gases, 773
 - government regulations relative to
 - pollution, 49
 - journals, 8
 - leaving heavy chemicals sector, 114
 - market entry, freedom of, 26–27
 - mergers, 56
 - monitoring, 28
 - national economy, 13–16
 - North American Industry Classification
 - system (NAICS), 5
 - organic chemical industry
 - to synthesize quinine, 96
 - overcapacity, 51
 - patents, 9–10
 - pervasiveness, 24–26
 - petroleum and refinery products, 773
 - pharmaceutical sector, 58, 59
 - R&D spending, 37
 - regulation of fracking industry, 102
 - research and development
 - expenditures, 34–41
 - restructuring, 56
 - shipments and value added in
 - manufacturing industry, 17
 - size of, 16–22
 - Southeast Asian chemical industry, 114
 - statistics/internet sources of
 - information, 10–12
 - strong regulation, 27
 - European legislation, 29–30
 - monitors, 28
 - political factors, 30–34
 - subdivisions of, 19
 - top chemical companies, 56–60
 - top chemicals, 44–46
 - top companies, 43–44
 - top 40 United States chemical
 - companies, 38–39
 - United States, 20–21
 - R&D spending, 36
 - units/nomenclature, 5–6
 - until World War II, 96
 - world chemical market, 18
 - world chemical sales by region, 51
- Chemical Industry, Europe*, 8
- Chemical Manufacturers' Association (CMA), 32
- Chemical sales, 50
 - by region, 51
- Chemicals transportation
 - methods, 77
 - Texas pipeline system, 75, 78
- China
 - climate change, 711
 - coal-based chemical industry, 97
 - coal exporter, 475

- China (*Continued*)
 coal-to-chemicals industry, 486
 economic miracle, 760
 Industrial Revolution, 761
 patterns of oil consumption, 96
 wages, 761
 wind turbines, 719
 Chinese government, 717
 Chiral syntheses, 661
 Chiyoda's process, 646
 Chlorinated benzenes, 363–364
 Chlorinated hydrocarbons, 742
 Chlorinated phenols, 342–343
 manufacture of, 755
 Chlorinated polymers, 32
 Chlorination
 of acetaldehyde, 190
 of ethylene dichloride, 203
 of vinyl chloride, 203
 Chlorine
 bleaching of paper, 44
 Chloroacetic acid, 442
 Chloroethane, 412
 Chlorofluorocarbons
 photolysis of, 738
 Chlorofluorocarbon solvents, 686
 Chloromethane, 413
 production, 412
 Choline, hydroxyl group of, 498
 Chlorofluorocarbons (CFCs)
 CHP installations, 731
 Chromic oxide, 599
 Chromium–carbon bonds
 formation of, 599
 Chromium hexacarbonyl, 443
 C₄ hydrocarbons
 pipelines, 77
 Clean Air Act, 135, 136
 Cleveland Discol, 136
 Climate change, 711
 Coal, 475
 calcium carbide, 488
 Chinese chemicals to coal
 program, 489–490
 chemicals and energy, 475
 and environment, 490–491
 Fischer–Tropsch process, 484
 Fischer–Tropsch reaction, 480–484
 gasification processes, 487
 hydrogenation, 484–485
 hydrogenation of, 476
 oven distillate, 477–480
 SNG/synthesis gas technology,
 485–488
 source of chemicals, 96
 substitute natural gas, 485
 synthesis of butadiene, 188
 underground coal gasification
 (UCG), 488
 Coal-based gas mixtures, 476
 Coal-based synthesis gas, 476
 Coal-fired power stations, 713
 Coal tar, 477
 distillation, 478
 Coal-to-dimethyl ether, 489
 Cobalt sulfide, 724
 Cocoa butter
 triglycerides, 513
 use of, 514
 world production, 515
 Cocoa butter extenders (CBEs), 514
 Coke, 477
 benzene from, 479
 used in steel manufacture, 477
 Coking, 105, 125, 126
 C₄ olefins, 309
 separation of, 274
 C₅ olefins, 309
 separation of isopentane from, 311
 C₄ olefins stream
 major components, 275
 separation of, 276
 Combinatorial chemistry, 676, 677
 Combined cycle gas turbine plants
 (CCGT), 488
 Combined heat and power (CHP)
 systems, 729
 use of, 729
 Combustion heat, 759
 Comonomer Production Technology
 (CPT), 483
 Lummus's CPT process, 483
 Competition, from developing countries, 66
 Complementary metal oxide semiconductor
 (CMOS) technology, 622
 Compression molding, 632
 Concentrated photovoltaics (CPVs), 722
 Concentrated solar power (CSP), 721

- Conduction band (CB)
 - of semiconductor, 723
- Congenital malformations, 755
- ConocoPhillips, 460
- Continuous catalyst regeneration reformers (CCRs), 120
- Continuously stirred tank reactors (CSTRs), 644
- Copolymerizing monomer, 577
- Copolymers, 589
 - of acrylonitrile, 230
 - block, 589, 591, 592
 - cyclic olefin copolymers (COCs), 320
 - ethylene, 151
 - ethylene-1-octene copolymers, 604
 - ethylene-vinyl alcohol copolymer, 440
 - from “incompatible” polymer blends, 152
 - of isobutene, 298
 - linear ethylene–propylene copolymer, 569
 - Spandex, 305
- Copper-containing catalyst, 698
- Copper–manganese oxide (CuO–MnO₂), 465
- Cost calculations, 765–769
 - cash costs, 768
 - cash flow, 767
 - chemical industry, accounting, 765
 - EBIT, 769
 - expenditure, 766
 - fixed costs, 765
 - income, 766
 - return on investment (ROI), 768
 - sunk cost approach, 768
 - total costs, 768
- Cough syrups, 413
- Coupling agents, 318, 473, 583, 662
- C₉ plasticizer, 303
- Cracking
 - catalytic cracking, 105
 - hydrocracking, 105
 - steam cracking, 105
- Creosote (heavy oil), 479
- Cresols, 343, 477, 479
- Crotonaldehyde, reaction with
 - ethanol, 188
- Crude oil distillation, 95
- Crystalline melting point, 627
- Crystalline polymers, 625
- Crystallinity, 622
- Crystallization
 - characteristics, 514
 - of cured rubber by stretching, 626
 - of molten resin as it cools, 396
- C₄ stream olefins, 102, 110, 274
- C₅ stream olefins, 215, 311, 319
- Cumene
 - mechanism of the cumene–phenol process, 233
 - oxidation of, 245
 - reaction with oxygen, 232
 - value chain, 232
- Cumene (isopropylbenzene), 231
- Cu–Ni catalyst, 205
- CuO/γ-Al₂O₃ promotes methanol
 - dehydration, 445
- Cu–Zn–alumina catalyst, 436
- Cyanogen hydrolyzes, 411
- Cyanuric chloride, 410
- Cyclar process, 471
- Cyclic olefin copolymers (COCs), 320
- Cyclization, of 2 and 3 moles of
 - butadiene, 289, 290
- 1,5,9-Cyclododecatriene, 292
- Cyclohexane, 99, 344, 654
 - adipic acid, 344–349
 - nylons from, 349
 - caprolactam, 349–354
- Cyclohexanone, 341–342
- 1,5-Cyclooctadiene, 290
- Cyclopentadiene, 319
- Cyclopentadienyl–zirconium–nitrogen bond
 - angle, 602
- Cyclopentene, 130, 654
- Cyclotrimethylene trinitramine, 433
- DABCO, 193, 649
- Dacron, 173
- Davy McKee process, 422
- DDT factory, 742
- 1,9-Decadiene, 291
- Decahydronaphthalene, 479
- Decalin. *See* Decahydronaphthalene
- Decarboxylation
 - catalytic decarbonylation/oxidation
 - followed by, 531
 - of intermediate dicarboxylic acid, 189
- Deep catalytic cracking (DCC), 215
- DEHP metabolizes, 390

- Dehydration
 - of acetaldehyde, 188
 - of crotonaldehyde, 188
 - of ethanol to ethylene, 150
- Dehydrobromination
 - of ethylene dibromide, 206
- Dehydrofluorination
 - 1,1-difluoroethane, converted to additional vinyl fluoride, 205
- Dehydrogenation, 105, 126–128
 - of alkylcyclohexanes, 122
 - 1- and 2-butenes, 303
 - catalyst, 654
 - convert isobutane to isobutene, 127
 - of cyclohexane, 122
 - of ethane, 127
 - to isoprene, 310
 - olefin–alkane mixture, 310
- Dehydrogenation/oxidation process, 438
- Dehydrohalogenation
 - with calcium hydroxide, 264
 - chlorination of vinyl chloride followed by, 203
 - of ethylene dichloride, 192
 - to give epichlorohydrin, 263
 - to provide ethylene oxide and calcium chloride, 170
 - yields vinyl fluoride, 204
- Demethanizer, 107
- Dendrimer encapsulated nanoparticles (DENs), 672
- Dendrimers, 615
 - properties of, 617
- Dendritic polymers, 613
- Deodorization, 499
- Desalination, 715
- Desulfurization, 428
- Detergents, 26, 183, 221, 519, 537, 664, 751
- 1,4-Diacetoxybutane, 421
- 1,4-Diaminobutane
 - reaction with adipic acid, 206
- Di- and triethylene glycols, 193
- Diazabicyclooctane (DABCO), 649
- Di-*t*-butyl peroxide, 574
- Dibutyl phthalate (DBP), 744
- 3,4-Dichlorobenzoyl chloride, 694
- 2,2-Dichlorodiethyl ether
 - condense to form 1,4-dioxane, 203
- Dichlorodifluoromethane, 739
- Dichloromethane (methylene chloride), 413
- Dichloromethane production, 413
- 2,4-Dichlorophenoxyacetic acid, 450
- Dicobalt octacarbonyl, 185
- Dicyano compound, 614
- Dicyclopentadiene, 319
 - oxidized to maleic anhydride, 321
- Diels–Alder condensation, 293
- Diels–Alder reaction, 269, 319, 504, 505, 686
- Diesel engines, 657
- Diesel fuel
 - prices, 133
- Diesel fuels, 517
- Diethanolamine, 698
- Diethanolamine (DEA)
 - demand, 198
- Diethylene glycol bis(allyl carbonate), 456
- Di(2-ethylhexyl) adipate, 258
- Di(2-ethylhexyl) phthalate, 387
- Di-2-ethylhexyl phthalate (DEHP), 388, 744
- Di(2-ethylhexyl)phthalate (DOP), 258
- Di(2-ethylhexyl) terephthalate, 258
- Difasol modification, 689
- Diffusion, 582
- 1,1-Difluoroethane, 205
- Digoxin, 696
- Dihydroxybenzenes, 364
 - catechol, 369–370
 - hydroquinone, 364–368
 - resorcinol, 368–369
- Dihydroxyphenylalanine, 660
- Diisobutenes, 130, 260, 297, 298, 342
- Diisononylcyclohexane dicarboxylate, 260
- Di-isononyl-cyclohexane dicarboxylate (DINCH), 390
- Di-isononyl phthalate (DINP), 388
- Dimer acid, 504, 505
- Dimer formation, 290
- Dimerization
 - of butadiene, 130
 - 1-butene, 154
 - ethylene, 154
- Dimersol, 124
- Dimersol process, 689
- Dimethylacetamide, 450
- Dimethylamine, 449
- 3,3'-Dimethylbiphenyl, 746
- 2,2-Dimethyl-1-butene, 130
- Dimethyl carbonate, 451, 685

- Dimethylcyclopentane, 99
- 4,6-Dimethyldibenzothiophene, 747
- 2,6-Dimethylnaphthalene, 296
- Dimethyl-2,6-naphthalene dicarboxylate
 - synthesis of, 295
 - uses, 295
- 3,3'-Dimethylphenyl, 747
- Dimethyl sulfoxide, 451
- Dimethyl terephthalate, 403
- Dioxane, use as solvent, 203
- Dioxin, 755
- Dioxolane, 202
- 4,4'-Diphenylmethane
 - diisocyanate, 357–361
- 4, 4' Diphenylmethane diisocyanate (MDI)
- Dipole–dipole forces, 628
- Direct methanol fuel cell (DMFC), 734
- Disposal, releases by industry, 737
- Distearyltrimethylammonium chloride, 503
 - use of, 502
- DL-Methionine hydroxy analog, 268
- Dodecylbenzenesulfonic acid, 618
- Dodecyl mercaptan, 576
- Domestic sewage, 750
- Double methanation process, 485
- Dow Chemical, 32
 - acquisition, 241
 - R&D spending, 37
 - as top chemical companies, 38
- Drying oil, 391
- DSM
 - for direct oxidation of propylene to propylene oxide, 249
 - funds for methane activation research, 465
 - process for dimerizing butadiene, 283
 - R&D spending, 37
 - as top chemical companies, 56
- DuPont, 422, 456
 - commercialization of a new polyester resin, 404
 - for hexamethylenediamine, 229
 - manufacture of 1,3-propanediol by fermentation of, 546
 - methyl methacrylate business and a cash payment, 60
 - objective, 201
 - patents., 27
 - process for nitration of cyclohexane to nitrocyclohexane, 463
- R&D spending, 37
 - required tetrahydrofuran for oligomerization, 305
- Selar, 152
- Surlyn, 152
 - synthesis, adiponitrile, 658
 - synthesis of adiponitrile, 658
 - transport bed, 304, 642
- Dye-sensitized solar cells (DSSCs), 722, 723
- Dynacracking, hydrotreating processes, 126
- Eastman Chemical
 - and Air Products, joint venture, 436
 - convert butadiene to corresponding monoepoxide, 296
 - R&D spending, 37
 - working with Halcon, 443, 444
- Eastman/Halcon acetic anhydride process, 452
- Eastman-modified Texaco gasifier, 444
- Economy
 - for chemical industries, 13–22
 - NAICS classification, 14
- Elasticity, 590
- Elastic memory, 625
- Elastomers, 278, 279, 282, 283, 630
- Electrochemical process, 691
- Electron deficiency, 596
- Electron micrographs, 642
- Eluxyl, 384
- Emanating, 623
- Emission catalysts, 657
- Emulsifying agent, 232
- Emulsion polymerization, 582
- Energy consumption, 557, 718
 - world population, 718
- Energy sources
 - methane hydrate, 727–728
 - nuclear energy, 726–727
 - solar energy, 721
 - artificial photosynthesis, 724–726
 - concentrated, 721
 - dye-sensitized solar cells (DSSCs), 722–724
 - photovoltaic cells, 721–722
 - wave power, 720
 - wind power, 719
- ENI, 39, 53, 56, 58, 59

- Environmental issues, 8, 11, 32, 33, 150, 204, 320, 417, 675, 698, 747, 756
- Environmental stress crack resistance (ESCR), 150
- Enzymatic amination, 458
- Enzymes, 661
- Epichlorohydrin, 263
 - converting glycerol to, 265
 - reaction with bisphenol A, 265
 - role in glycerol synthesis, 265
 - Showa Denko epichlorohydrin process, 264
 - synthetic routes to, 265
- Epoxidation, 174, 190, 246, 251, 303, 510, 661
 - of soybean oil, 190
- Epoxidized soya oils, 510
- Epoxidized soy oil, 509, 510
- Epoxy groups, 612
- Epoxy resins, 333, 611
 - polymer molecule of, 612
 - uses, 334
- Erucic acid, 500
- Essential Chemical Industry, The*, 8
- Esterification, 395
- Esters, 195, 222
 - commercially important, 195, 196
 - properties, 197
- Ethane
 - aromatization of, 471
 - chlorination of, 186, 187
 - dehydrogenation of, 470, 471
 - oxychlorination of, 468
- Ethanol, 42, 181, 182
 - as chemical feedstock, 68
 - with copper, 639
 - corn-based fermentation ethanol for fuel, 68
 - derivatives, 206–207
 - production, 112
 - as renewable resource, 136
 - used as motor fuel, 135
- Ethanolamines, 107
- Ethanolamines end uses, 198
- Ethanol hydrogen chloride
 - rhodium chloride, dilute solution, 658
- Etherification, process to MTBE, 276, 297
- Ethers, 207, 208
- Ethyl acetate, 168, 182, 440, 443
- Ethylamines, 142, 206, 207
- Ethylbenzene hydroperoxide, 463
 - decomposed with nickel catalyst to, 329
- Ethylbenzene, oxidation of, 463
- Ethylene
 - capacity and production, 52
 - end-use patterns, 143
 - global ethylene capacity, 54
 - annual addition., 53
 - global ethylene production and consumption patterns, 184
 - home-produced, 114
 - lesser volume chemicals from, 185
 - major chemicals and polymers from, 141, 182, 183
 - from naphtha, 113
 - oligomerization, 321
 - oxo/hydroformylation reaction with, 185
 - oxychlorination of, 649
 - pipelines, 77
 - polymerization of, 580
 - polymers, 141, 142
 - production, 448
 - in five regions, 50
 - and price ratios, 214
 - proton-catalyzed hydration of, 646
 - return on sales of major ethylene producers over time, 55
 - for shipment, 113
 - steam cracker operating rates, 52
 - trimerization, to 1-hexene, 157
 - undergo metathesis, 130
- Ethylene carbonate
 - preparation, 197
 - use as intermediate in ethylene glycol and dimethyl carbonate formation, 197
- Ethylene chlorohydrin
 - condense to form 1,4-dioxane, 203
- Ethylene copolymers, 151
 - chlorosulfonated polyethylene, 151
 - copolymer from “incompatible” polymer blends, 152, 153
 - ethylene–propylene elastomers, 153
 - ethylene-vinyl acetate, 151, 152
 - ionomers, 152
 - polyolefin elastomers, 153, 154
- Ethylene cracker
 - VCM/PVC production, 468
- Ethylenediamine, 612

- reaction with ethylene oxide, 193
 - and related compounds, 191–193
- Ethylenediamine tetraacetic acid (EDTA), 410
 - hydrolysis of, 410
 - nitrile, hydrolysis of, 410
- Ethylene dibromide, 205, 206, 670
- Ethylene dichloride
 - oxychlorination of, 423
- Ethylene glycol, 171–174, 400, 454, 489
 - derivatives, 193, 202
 - non-ethylene oxide processes for, 174–177
- Ethylene glycol ethers, 195
 - commercially important, 195, 196
- Ethylene glycol monoethyl ether, 194
- Ethyleneimine
 - preparation, 199
- Ethylene-1-octene polymer, 602
- Ethylene oligomerization technologies, 156
- Ethylene oxide, 169–171, 193
 - commercial development of, 639
 - condense to form 1,4-dioxane, 203
 - potential energy diagram for, 640
 - reaction with alcohols, 194
- Ethylene propylene diene monomer (EPDM)
 - rubber, 592
- Ethylene–styrene copolymers, 602
- Ethylene-to-butene ratio at reactor, 129
- Ethyl halides, 186
- 2-Ethylhexanol, 258, 259, 260
 - end-use pattern of, 258
- 2-Ethylhexanol
 - demand, 259
- Ethyl *t*-butyl ether (ETBE), 136, 297
 - in unleaded gasoline, 136
- Europe
 - cost of diesel fuel, 133
 - Danube as waterway for transport of chemicals, 79
 - dependent on pyrolysis gasoline, 113
 - pipeline network, 113
 - synthesis of butadiene, 188
 - trade balance, 64
 - transport of petroleum, 75
- Extracellular microbial enzymes, 662
- Extrusion, 633
 - blow, 633
 - production of film, 634
- ExxonMobil, 106, 460
- Fats and oils, 493
 - alcoholysis of, 513
 - algae, 518
 - biodiesel, 516–518
 - cocoa butter, 513–515
 - interesterification, 515–516
 - lubricants, 516–518
 - mothers' milk, 515
 - trans* fats, 515–516
 - alkyl polyglycosides, 519
 - aminoamides, 506–507
 - application of, 506
 - azelaic, 507
 - chemical reactions of, 499
 - crystalline structure of, 493
 - dimer acid, 504–506
 - enzymatic hydrolysis, 500
 - epoxidized oils, 509–510
 - fatty acids, 494
 - and glycerol, 508
 - production, 499
 - applications of, 501–502
 - fatty alcohols, 508–509
 - fatty nitrogen compounds, 502–504
 - glycerol, 512
 - established uses, 512–513
 - imidazolines, 506–507
 - markets for, 494–497
 - non-caloric fat-like substances, 519–520
 - pelargonic, 507
 - petroselinic acids, 507
 - purification of, 497–499
 - ricinoleic acid, 510–512
 - U.S. consumption, 496
 - world production, 495
- Fatty acid methyl esters (FAMEs), 393, 516
- Fatty acids, 494
 - hydrogenolysis of, 508
 - microbial conversion of, 502
 - sodium salts of, 498
- Fatty alcohols, 509
- Fatty ethanolamide, as foam stabilizer in detergent formulations, 198
- Fatty nitrogen chemistry, 503
- Fatty nitrogen compounds, 506
- Federal landfill standards, 757
- Feedstock, choice of, 108

- Fermentation
 - Brazilian alcohol made by, 135
 - ethanol as a gasoline additive, 68
 - use of fermentation alcohol, 136
- Fertilizers, 32
 - inorganic and organic chemicals, 45
- Fischer-Tropsch reaction, 458, 459, 476, 480, 482, 484, 666
 - make diesel fuel, lubricants, and wax, 133
 - mechanism of, 481
 - Sasol's application of, 459
- Fischer-Tropsch Synthol fuel stream, 482
- Fischer-Tropsch waxes, 481, 502
- Fisher-Tropsch liquids, 429
- Fish oils, 501
- Flue gas desulfurization, 746
- Fluidized-bed hard-coal gasification
 - plant, 446
- Fluidized beds, 644, 646
- Fluorinated ethers, 414
- Fluorocarbons, 414
 - applications and replacements, 416
- Fluorous biphasic catalysis, 670
- Fluorous rhodium-catalyzed alkene
 - hydrogenation, 671
- Formaldehyde
 - end-use patterns, 437
 - polymers, 571
- Formic acid, 455
- Formica-type decorative laminates, 635
- Formosa Plastics, Sinopec, 53
- β -Formylcrotyl acetate, 659
 - synthesis of, 659
- Free energy of activation, 641
- Free radical initiation, 584
- Free radical polymerization, 573
- Friedel-Crafts catalyst, 122, 124, 231, 298, 480, 643, 651, 653, 686
- Fuel cell
 - maximum efficiencies, 730
 - Carnot, 730
 - types of, 731–732
- Fusion reactors, 727
- Gallium-doped H-form zeolite, 467
- Gas cracking economic, propylene not in
 - short supply, 112
- Gas diffusion electrode, 731
- Gas emissions, 757
- Gases landfill, percentage composition, 757
- Gas oil, 472
- Gasoline, 482
 - alcohol used in, 136
 - benzene, elimination of, 33
 - hydrophobicity, 136
 - industry, 64
 - to maintain octane number of, 135
 - natural, 110
 - prices, 133
 - propylene, 1- and 2-butenes uses in, 303
 - pyrolysis gasoline, 99, 106
 - unleaded, 134
 - and clean air act, 134–136
 - vs. methanol, 446
- Gasoline-range hydrocarbons, 557
- Gas-to-liquid (GTL) process
 - technology, 459, 460
- General Agreement on Trade and Tariffs (GATT), 114
 - regulations., 11
- Germany
 - chemical companies, 60
 - coal tar, 480
 - pharmaceuticals from “renewables,” 696
 - wind power, 719
- Glass transition temperature, 626, 627
- Global ammonia consumption, 432
- Global warming, 708, 710, 728
 - carbon dioxide pollution, 718
 - efficiencies of gases, 709
 - nuclear energy, 726
- Glutaraldehyde, 269
- Glycerol, 265, 501, 512, 513, 568
 - esters of, 493
 - manufacture, 266
 - synthesis, 266
- Glycerol monoesters, 513
- Glyceryl trinitrate (nitroglycerin)
 - adsorbed on wood pulp, 512
- Glycol ethers, 194, 456
 - esterified with acetic acid, 194
 - global market for, 197
 - properties, 197
- Glycolic acid, esterification of, 454
- Glycols, 568
 - for dehydration of natural gas, 194
- Glyoxal, 201
- Gold nanoparticles, 671

- Gold–palladiumnanoparticles, 672
- Good Manufacturing Practice (GMP), 27
- Graft copolymers, 593
- Graphene, 620
- Green chemistry, 681
 - acetylene chemistry, decline of, 683
 - biodegradable packaging, 698
 - polyhydroxyalkanoates, 701–703
 - production of polymers, 699
 - properties of, 700
 - challenges, 703–704
 - diethanolamine, catalytic dehydrogenation of, 698
 - genetic manipulation, 698
 - industrial chemical processes,
 - environmental implications, 681
 - ionic liquids, 687–690
 - liquid/supercritical carbon dioxide/
 - water, 685–687
 - monomethylation, by dimethyl
 - carbonate, 685
 - nylon 6, production of, 683–684
 - paired electrosynthesis, 691–692
 - pharmaceuticals
 - ibuprofen, 692–694
 - renewables, 696–698
 - sertraline, 694–696
 - phosgene replacement, 684–685
 - photocatalysts, 690–691
 - twelve commandments of, 682
- Greenhouse effect, 708
- Greenhouse gas emissions
 - from fossil fuel, 712
 - by top ten emitters, 712
- Green methanol process, 728
- Green polyols, 510
- Gross disposable product (GDP), 14
- GTL technology, 459
- Gum formulation, 593
- Gypsum, 745

- Haber process, 430, 431, 655, 674
- Halogenated methanes, 411
- Halogen atoms
 - destruction of ozone, 739
- Head-to-tail polymerization, 575
- Heavy oils, fractions, 103, 104
- Heck reaction, 689
- Henkel I process, 400

- Heptamethylbenzenium cation, 448
- 1,5-Hexadiene, 292
- Hexamethylenediamine, 284–289
 - DuPont’s process, 26
 - hydrogenated to, 285
 - routes, start with butadiene, 284
- Hexamethylenediamine, role in production of
 - nylon 66, 289
- Hexamethylenediisocyanate (HMDI), 611
- Hexamine, 439
- 1-Hexene, 655
- Hexene-3, 483
- HF/BF₃ catalyst system, 382
- High density polyethylene (HDPE), 578
- Himalayan glaciers, 710
- Hippuric acid, 743
- HMDI biuret trimer, 609
- Hooke’s law, 628
- Huntsman Chemical Corporation, 61
- Hydrocarbon, feedstock, 106
- Hydrocarbon fractions
 - catalytic cracking of, 642
- Hydrocarbon gases, 719
- Hydrocarboxylation
 - of isobutene via Koch reaction, for pivalic acid, 301
- Hydrocracking, 105
- Hydrocyanic acid, 409, 410
- Hydrodemetallization, 137
- hydrodenitrogenization, 137
- Hydrodesulfurization, 126, 137
- Hydrofluoric acid (HF), 414
- Hydrofluorocarbons, 414
- Hydrofluorocarbons (HFCs), 739
- Hydroformylation, 421
 - C₆–C₁₂ olefins, 260
 - of internal olefins, 160
 - linear, 256
 - of propylene, 188
 - of Raffinate II, 303
 - reaction with ethylene producing
 - propionaldehyde, 185
- Hydrogenation, 457, 498, 499
 - of 1,5-cyclooctadiene, 130
 - of 3-hydroxypropionaldehyde, 269
 - of isophorone, 242
 - isopropanol made by, 328
 - mesityl oxide to methyl isobutyl ketone, 242

- Hydrogenation (*Continued*)
n-butyraldehyde, 258
 of succinonitrile, 206
 Hydrogenation/dehydrogenation catalyst
 (Pt), 654
 Hydrogen bonding, 194, 628
 Hydrogen chloride, 739
 Hydrogen cyanide, 411
 Hydrogen cyanide (HCN), 408
 propylene, ammoxidation of, 409
 sodium salt, 409
 United States, 408
 Hydrogen Fuel Initiative (HFI), 735
 Hydrogenolysis, 489
 Hydrogen-rich synthesis gas, 481
 Hydrolysis, 409
 Hydrometallurgical techniques, 713, 726
 Hydroquinone, 576, 577
 Hydroquinone monomethyl ether, 300
 Hydrothermal synthesis, 666
 Hydrotreating, 105, 125, 126
 development, 126
 used for refining of lubricating oils, 126
 of vacuum gas oil, 126
 Hydrotreating catalysts, 654
 Hydroxyepoxide, 663
 4-Hydroxyphenylglycine, 201, 202
 β -Hydroxypropionaldehyde, 200
- Ibuprofen, Boots synthesis of, 692
 Imidazolines, 506
 Immobilization, 662
 Indium tin oxide (ITO), 726
 Indium tin oxide electrode, 620
 Inert gases, discoverer of, 712
 Institute of Scientific Information (ISI), 11
 Intergovernmental Panel on Climate Change
 (IPCC), 708, 711
 Internal Revenue Service and
 legislation., 765
 International Union of Pure and Applied
 Chemistry (IUPAC), 6
 Ionic initiators, 585
 Ionic liquids, 687, 688, 689
 Ionic polymerization, 584–589
 Iron-based catalysts, 431
 Iron catalyst, 415
 Iron phosphate, 752
 Irrigation, 715
- Isobutane
 alkylation of, 651
 in presence of Friedel–Crafts
 catalysts, 124
 Isobutene, 191, 273
 chemicals and polymers from, 296–297
 butyl rubber, 298
 isobutene oligomers, 298, 299
 lesser volume chemicals from
 isobutene, 299–302
 methyl methacrylate, 299
 methyl *tert*-butyl ether, 297–298
 polyisobutenes, 298, 299
 polymers, 298, 299
 tert-butanol, 299
 reaction with methanol to produce, 115
 sources of, 135
 Isobutyraldehyde, 255, 259
 uses for, 258–259
 Isocyanate, 611
 Isocyanate-terminated prepolymer, 590
 Isomeric polybutadienes, 597
 Isomerization, 105, 128
 to branched compounds increasing octane
 number, 99
 1-butene, 303
 of C₅/C₆ alkanes for gasoline pool, 128
 to increase octane rating of C₅/C₆
 alkanes, 128
 Isopentenes, 310
 reaction with methanol to produce, 115
 Isophorone diisocyanate, 610, 684
 Isoprene, 312
 applications, 317–319
 2-methyl-1,3-butadiene, 312
 natural rubber, 312–313
 precursor results from metathesis of
 isobutene, 131
 production of petrochemical
 isoprene, 314–317
 by dehydration of 2-methylbutanal, 317
 styrene–isoprene–styrene (S-I-S)
 block, 318
 trans-1,4-polyisoprene, 319
 vulcanization, 313, 314
 Isopropanol, 233
 Mitsui Chemical, development of
 process, 234
p/o-Isopropyltoluene, 653

- ISOtanks, for transport of chemicals, 81–83
- Israel, solar energy, 722
- Japan
 - ARCO process developed further by, 357
 - chemical industry, based on imported naphtha, 65
 - cost of diesel fuel, 133
 - demand for gasoline, 94
 - ethylene market, 102
 - ethylene production in, 50
 - industries, 49
 - profitability, 59
 - patterns of oil consumption., 96
 - polycarbonate plant in, 335
 - use for oxalic acid, 458
- Koch acids, 424
- Kolbe-Schmidt reaction, 686
- Leblanc process, 681
- Levodopa
 - Monsanto's asymmetric synthesis of, 660
- Lewis acids, 588, 651
- Light-emitting electrochemical cell, 621
- Linear alkylbenzene (LAB), 652
- Linear low density polyethylene (LLDPE), 578
- Linear polymers, properties of, 617
- Linoleic acid, 392, 500
 - dimerization of, 504
- Linolenic acid, 392
- Lipophiles, 743
- Liquefied natural gas, 98
- Liquefied natural gas (LNG), 459
- Liquefied petroleum gas, 98
- Liquefied petroleum gas (LPG), 471
- Liquid carbon dioxide, 686
- Liquid crystal display (LCD), 242
- Liquid petroleum gas (LPG), 518
 - used in petrochemical plant, 69
- Lithium phosphate catalyst, 421
- Living polymers, 589
- London dispersion forces, 628
- Los Angeles smog cycle, 749
- Low density polyethylene (LDPE), 578
- Low-VOC, alkyd – acrylic dispersion (LAAD), 393
- Lurgi process, 487
- Lurgi's MTP (methanol-to-propylene) process, 447
- LyondellBasell Industries (LBI), 63
- Maleic anhydride, 362, 392, 577
 - butane, oxidized to, 136
 - end-use pattern, 305
- Malonic ester synthesis, 457
- Marasse modification, 686
- Megamethanol plants, 436
- Melamine, 434
- Melamine-formaldehyde (M/F) resins, 435
- Mercury cells, 712
- METabolic Explorer, 512
- Metabolix, 702
- Metal complexes, 191
- Metallocene-based polyolefin catalysts, 602
- Metallocene-based single site, 599
- Metallocene catalysts, 40, 601, 604, 641
- Metallocene LLDPE resins, 604
- Metallocene polypropylene, 604
- Metallocenes, 600
- Metal–organic frameworks (MOF), 668
- Metathesis, 42, 128, 129
 - of 1,5,9-cyclododecatriene, 292
 - mechanism, 131, 132
 - outside refinery, 129–131
- Methacrylaldehyde, 299
- Methane/oxygen mixtures, 756
- Methane Princess*, 75
- Methanes, 108, 407, 429, 709, 729
 - acetylene, 417
 - 1-4-butyne diol, 419–423
 - lesser uses for, 423–424
 - 2-methyl-1,3-propanediol, 419–423
 - Wulff process, 418
- ammonia, derivatives, 430
 - ammonia manufacture, 431–434
 - nitrogen depletion, crisis of, 430–431
 - urea/melamine resins, 434–435
- aromatization of, 464
- based chemical, 415
- carbon monoxide chemistry, 454
 - carbon monoxide, proposed uses of, 455–459
- catalytic oxidative coupling of, 466
- C–H bonds, 464
- gas-to-liquid fuels

Methanes (*Continued*)

- GTL technologies, 460
- Sasol GTL technology, 459
- Shell Middle Distillate
 - Synthesis, 459–460
- halogenated methanes, 411
 - bromomethane (methyl bromide), 416–417
 - carbon disulfide, 414–416
 - chloromethane, 412–413
 - dichloromethane, 413
 - fluorocarbons, 414
 - tetrachloromethane (carbon tetrachloride), 414–416
 - trichloromethane (chloroform), 413–414
- hydrate
 - structure, 727
- methanol
 - acetic (ethanoic) acid, 439–442
 - acetic anhydride, 442–445
 - BP/Kvaerner, 436
 - capacity shift of, 437
 - C_7 -based development
 - processes, 452–454
 - formaldehyde, 438–439
 - formaldehyde end-use patterns, 437
 - to gasoline, 445–446
 - lower volume uses for, 448–452
 - to olefins, 446–448
 - synthesis gas, 435
 - oxychlorination of, 467
 - synthesis gas, 424
 - hydrocarbons, partial oxidation of, 428
 - hydrogen, 429
 - solid feedstocks, 428–429
 - steam reforming of, 425–427
 - steam reforming, variants of, 427–428
 - uses of, 407
 - yields
 - chlorination of, 411
- Methanol, 42, 435, 452, 453, 464, 729
 - dehydrogenation/oxidation of, 438
 - global
 - end-use patterns, 437
 - as neat automotive fuel, 136
 - olefins, formation of, 449
 - plants
 - capacity shift of, 437
 - world methanol trade, 80
 - Methanol to olefins (MTO), 217, 446
 - light olefin production, comparison of, 447
 - Methanol-to-propylene (MTP) process, 217
 - DL-Methionine, synthesis of, 410
 - Methyl acetate, 452
 - Methylaluminioxanes, 601
 - Methylamine, 450
 - Methylation
 - by dimethyl carbonate, 683
 - Methyl bromide, 33, 740
 - replacements for, 741
 - Methyl bromide pollution, 741
 - 3-Methyl-1-butene, 297
 - Methylbutenes, 310
 - Methylcyclopentane, 99, 654
 - Methyldecahydronaphthalene, 99
 - N*-Methylimidazole, 689
 - Methyl iodide, 741
 - Methyl isobutyl ketone, 242
 - acetone reactions, 243
 - Methyl isocyanate, 450
 - Methyl methacrylate, 235–241
 - by-product problem, 235
 - dehydration and hydrolysis of the nitrile group, 235
 - global consumption, 241
 - ICI process, developed jointly with, 235
 - Mitsubishi Gas Chemical Company
 - process for, 235
 - process under development by, 240
 - Evonik IndustriesAG, 240
 - Shell, 240–241
 - sodium hydroxidecatalyzed condensation, 235
 - syntheses, 236
 - C_4 ammoxidation, 239
 - conventional route, 239
 - C_4 oxidation, 239
 - ethylene-based, 239
 - methylacetylene-based, 240
 - Mitsubishi route, 239, 241
 - propylene-based, 239, 240
 - usages, 241
 - Western Europe demand pattern, 241
- Methylolureas, 606
- Methyl *t*-amyl ethers, 115
- Methyl *tert*-butyl ether (MTBE), 134, 273, 296, 297

- contaminating groundwater, 135
- isobutene for production, 135
- to maintain octane number of, 135
- Metric tons oil equivalent (MTOE), 717
- Microporous aluminosilicate minerals, 664
- Mitsubishi Gas Chemical, 40, 235, 238, 336, 455
- Mixed C₅ stream
 - conceptualized scheme for separation of, 311, 312
 - distillation, 312
 - ExxonMobil, development of catalyst, 312
 - isoprene, removal, 312
- Mobil olefin interconversion (MOI)
 - process, 217
- Mobil processes, 377, 446, 485, 666, 667
- Molding
 - compression, 632
 - injection, 632
- Monoglyceride, 392
- Monsanto process, 440
- Monsanto's methanol carbonylation
 - process, 439
- Morpholine
 - from dehydration of diethanolamine with sulfuric acid, 199
- Mosquito eradication program, 742
- MTG plant, 407
- MTG process, 446
- MTO plant, 407
- Municipal solid waste, 753
- Nafion* polymer, 730
- NAICS-based code
 - manufacturing category, breakdown of, 15
- Naphtha
 - catalytic reforming of, 323
 - contains aliphatics and cycloaliphatic materials, 99
 - cracked naphtha from refineries, 49
 - demand for gasoline, 111
 - feedstocks steam cracking, 106
 - versus* gaseous feedstocks, 102, 103
 - heavy naphtha, 99
 - light naphtha, 99, 110
 - for manufacture of olefins, 94
 - steam naphtha cracker, flowsheet for, 109
- Naphthalene, 386, 479, 484
- 2,6-Naphthalene dicarboxylic acid, 296
- Natural gas, 98
 - European, from North Sea contain, 112
 - flared/vented annually, 98
 - liquids, 98
 - separation of, 136
 - steam cracking
 - and catalytic reforming, 100
 - far less C₄ fraction, 274
- n*-Butane
 - chemicals from, 303
 - acetic acid, 303
 - maleic anhydride, 303–306
 - succinic, malic, fumaric, and tartaric acids, 306–307
 - direct blending into gasoline, 115
 - isomerization of, 128
 - oxidation of, 304
- n*-Butanol
 - demand, 259
 - propylene-based, 260
 - uses for, 258–260
- n*-Butenes, 302
- n*-Butyraldehyde, 255
 - with cobalt catalyst, 256
 - collaboration
 - between Union Carbide, Davy McKee, and Johnson Matthey, 256–257
 - hydrogenation of, 258
 - oxo process/hydroformylation, 256
 - undergo aldol condensation, 258
 - uses for, 258–260
- Neopentyl glycol (2,2-dimethyl-1,3-propanediol), 259
- Nickel carbonyl catalyst, 186
- Nickel catalyst, 258
- Nickel hydride catalyst, 158
- Nitrilotriacetic acid, 409, 439
- Nitrobenzene, 433
- Nitrocyclohexane, 433
- Nitrogen dioxide, 749
- Nitrogen, heats of adsorption, 655
- Nitrogen–phosphorus–potassium (NPK) fertilizers, 44
- Nitrous oxide, 464, 709, 740
 - by-product of modern adipic acid production, 330
 - as greenhouse gas, 330
 - production, 331

- Noble metals, 772
- Non-caloric fat-like substances, 519–520
- Nonsteroidal anti-inflammatory agent, 653
- North American Industry Classification system (NAICS), 5
- Nova's Advanced Sclairtech reactor technology, 603
- Novolacs, 605
- NPC Iran, 53
- n*-Propanol
 - reaction with ammonia, 185
 - as solvent, 185
- Nuclear energy, 717
- Nuclear fusion, 728
- Nylon 4,6, 349
- Nylon 6, 344, 345, 349
- Nylon 6,6, 231, 289, 344, 627
- Nylon 11, castor oil production, 511
- Occupational Safety and Health Administration (OSHA), 87
- Octadecylaminopropionitrile, 270
- Octane number, 99
 - defined, 124
 - straight run gasoline, 99
- Oil
 - consumption, patterns of, 96
 - from tar sands, 137
- Oil-based paints, 391
- Oil-producing countries, 496
- Oils. *See* Fats and oils
- Oilseeds, 496
- Olefins, 452, 481
 - in MTO plant, 407
 - oligomers, 231
 - for polymer gasoline, 133
- α -Olefins, 458
 - formation of, 449
- Oleic acid, 505, 507
- Olestra, structure of, 520
- Oligomeric polyethylene glycols, 194
- Oligomerization, 122–124, 232
 - advantage of, 123
 - butene, 260
 - ethylene, 154, 158
 - with propylene, 1- and 2-butenes, and isobutene, 122
- Oligomers, 105, 122, 142, 194, 231, 357, 572, 573
 - ethylene oxide oligomers, 193, 194
- Omega acids, 493
- Organic chemicals, sources of, 94
- Organic light emitting diodes (OLEDs), 620
- Organophosphorus pesticides, 742
- Oxalic acid ester on hydrogenolysis, 458
- Oxamide, 410
- Oxidation
 - of aldehyde, 260
 - catalysts, 649
 - of 2-methyl-5-ethylpyridine with nitric acid, 189
 - nitric acid, 242
 - of propylene to allyl alcohol, 380
 - of propylene with cumene hydroperoxide, 233
 - of toluene, 380
- Oxinol, 136
- Oxo alcohols for surfactants, 260
- Oxo catalysts, 261, 303
- Oxo technology, 258
- Oxychlorination, 161, 327, 467, 468, 649
- Oxygen-poor environment, 657
- Oxygen, steel industry and for welding, 44
- Ozone depleting substances, 415
- Ozone layer, 738
- Ozonolysis, 507
- Palladium acetate, 457
- Palladium acetylacetonate, 457
- Palmitic acid, 515
- Palm oil, 514, 516
- Palm oil yields, 496
- Paraffin candles, 501
- Paraffins, 666
- Paraformaldehyde, 570
- Parcel tanker TMS Roland Essberger., 83, 84
- partial oxidation (POX)
- Patents and Design Journal (PDJ), 10
- Pelargonic acids, 507
- PEMFC, structure of, 730
- Pentaerythritol, 260
- 1,1,1,3,3-Pentafluoropropane (HFC-245fa), 611
- Pentene-1, 321
 - potential application as comonomer, 321
- Pentenomer, 130
- Perchloroethylene, 423
- Perkin's dye, 97

- Peroxyacyl nitrates (PANs), 747, 749
- Peroxyesters, 573, 574
- Persistent bioaccumulative toxic chemicals (PBTs), 736
- Pesticide, 685
- Petrochemical industry, 280
- Petroleum
 - distillation, 97–100, 137
 - crude oil distillation, 98
 - like fuels, 476
 - production, by-product of, 408
 - refining catalysts, 648
 - refining industry, 23, 24
 - refining reactions, 104, 105
 - and steam cracking, 105
 - reserves, 96
 - shortages, 97
 - transport, method, 71
 - cost factor, 73
 - pipelines, 73, 74
 - tankers, 73, 74
 - wax fractions, lubricating oil
 - dewaxing, 470
 - worldwide flows of oil, 72
- Phase-transfer catalysis, 669
- Phenol-formaldehyde resins, 565, 653
 - preparation of, 439
- Phenolic resins (phenoplasts)
 - types of, 605
- Phenolic resins, major applications, 331–332
- Phenolphthalein, 394
- Phenols, 326, 576
 - applications
 - as bisphenol A, 333
 - epoxy resins, 334
 - in fabrication of laminates, 332
 - manufacture of phenol–formaldehyde resins, 331
 - phenol end-use pattern, 332
 - phenolic moldings, 332
 - polycarbonate resins, 334–337
 - Asahi Chemical process, 330
 - in coal tar, 326
 - conversion of benzoic acid to, 328
 - ethylbenzene hydroperoxide decomposed
 - with a nickel catalyst, 329
 - processes development
 - cumene process, 328
 - by Korea Research Institute of Chemical Technology, 331
 - for phenol manufacture, 327
 - Raschig-Hooker regenerative process, 327, 328
 - Solutia phenol process, 330
 - Wacker reaction, 329
- Phenoxy herbicides
 - manufacture of, 755
- Phenoxy radical, 576
- Phenylacetic acid, 457
- m*-Phenylenediamine, 396
- Phillips Petroleum Company, 129
- Phillips process, 580
- Phosgene, 335
 - use of, 684, 685
- Phosphates, 409
- Photochemical smog cycle, 748
- Photodegradable polymer, 701
- Photoinitiators, 583
- Photosynthetic method, 518
- Photovoltaic cells, 724
- Phthalic anhydride, 393
- Phthalic anhydride end-use pattern, 387
- Phthalide, 692
 - electrosynthesis of, 691
- Phthalocyanine dyes, 395
- β -Picoline, 443
- Piperylene, 321
- Piperylene (1,3-pentadiene)
 - uses, 321
- Pivalic acid, 302
 - glycidyl esters, use in coatings
 - formulations, 302
 - hydrocarboxylation of isobutene via Koch
 - reaction, 301
- Plant cell culture, 696
- Plant polysaccharide, 557
- Plasticizer esters, 258
- Plasticizers, 259, 388
 - service requirements for, 388
- Plastics fabrication techniques, 631–635
 - blow molding, 633–634
 - calendaring, 634–635
 - casting, 632
 - compression molding, 631–632
 - extrusion, 633
 - injection molding, 632–633
 - laminating, 635

- Plastics fabrication techniques (*Continued*)
 transfer molding, 632
 vacuum forming, 634
- Plastics recycling, 400
- Pollution
 government regulations, 49
 by MTBE, 135
 radioactive contamination, 101
 reducing carbon dioxide emissions, 97
- Polyacetal resins, 439
- Polyacetals. *See* Formaldehyde polymers
- Polyacrylonitrile chains, 592
- Polyalkanoate, 702
- Polyalkylbenzenes, 231
- Polyalkylthiophenes, 618, 619
- Poly(amidoamine) dendrimers
 (PAMAM), 615, 672
- Polybenzimidazoles, 396
- Polybrominated biphenyls (PBBs), 743
- Polybrominated diphenyl ethers
 (PBDEs), 743
- Polybutadiene, 591
- Polybutadienes, 282
- Poly(butylene terephthalate), 403
- Polycarbonate resins, 334
 application for, 336–337
 conventional route to, 334
 development of process
 Asahi Chemical, 336
 Shell technology, 336
 disadvantages of melt process, 335
 preparation, without phosgene, 336
 transesterification process, 335, 336
 use for phase transfer catalysis, 334
- Polycarbonates, 624
 preparation of, 669
- Polycondensation polymer, 572
- Polyester consumption, 394
- Polyesterification, 571
- Polyester polyols, 422
- Polyether dendrimer films, 616
- Poly(ether imide), preparation of, 339
- Polyethylene, 114
 green, 150
 high density, 146, 147
 linear low density, 147, 148
 low and high density, 142
 low density, 144–146
 metallocene, 149
 very high molecular weight, 148, 149
 very low density, 149
- Poly(ethylene oxide) side chains, 593
- Poly(ethylene terephthalate), 399, 623
 glass transition temperature, 627
 Mylar sheet, 624
- Polyhydroxyalkanoates, 701
- Polyhydroxybutyrate, 702
- Polyimides, 572
- Polyimide synthesis, 571
- cis*-1,4-Polyisoprene, 595
- Poly(lactic acid) (PLA), 702
- Poly(lactide) biodegrades, 703
- Poly(lactide), melting point of, 703
- Polymer chain, 575
- Polymer crystallization, 623
- Polymeric plasticizers, 389
 production of, 572
 tributyl citrate, uses, 389
- Polymerization, 124, 565–568, 580, 582
 catalysts, global market for, 648
 to *cis*-1, 4-polyisoprene, 317
 of ethylene oxide with an iron catalyst, 194
 ionic initiators, 584
 of isobutene to polyisobutene, 276
 methods of, 584
- Polymerizing monomers, methods of, 586
- Polymer matrix, 621
- Polymer poly (3,4-ethylenedioxythiophene)
 poly(styrenesulfonate) (PEDOT:
 PSS), 620, 621
- Polymer properties, 630
- Polymers, 561. *See also* Polymerization
 applications of, 563–564
 chain growth polymerization
 ethylenic double bond, 568
 classes of, 630–631
 functionality, 568–571
 molecular weight of, 579
 plastics fabrication techniques, 631–635
 blow molding, 633–634
 calendaring, 634–635
 casting, 632
 compression molding, 631–632
 extrusion, 633
 injection molding, 632–633
 laminating, 635
 transfer molding, 632
 vacuum forming, 634

- properties
 - crystallinity, 622–626
 - glass transition temperature, 626–627
 - molecular cohesion, 628
 - stress–strain diagrams, 628–630
- step/chain growth
 - polymerization, 571–573
 - block copolymers, 589–592
 - chain transfer, 575–577
 - conducting polymers, 617–621
 - conducting/semiconducting
 - inks, 621–622
 - copolymerization, 577–579
 - dendritic/hyperbranched
 - polymers, 613–617
 - epoxy resins, 611–613
 - free radical polymerization, 573–575
 - graft copolymers, 592–593
 - ionic polymerization, 584–589
 - living polymers, 589
 - metal complex catalysts, 593–598
 - metallocene-based single site, 599–605
 - metal oxide catalysts, 598–599
 - molecular weight, 579–580
 - phenoplasts, 605–606
 - photoinitiation, 582–584
 - polymerization procedures, 580–582
 - polyurethanes, 606–611
- T_g and T_m values, 627
- three-armed star-shaped, 588
- unsaturated polyester resins, production
 - of, 569
- U.S. polymer production, 562, 565
- Poly(methyl methacrylate), 574, 624
- Poly(*p*-phenylene vinylene), 620
- Polypropylene, 219, 647
- Poly(propylene glycol), 608
- Poly(propyleneimine)
 - Vögtle's synthesis of, 613
- Poly(propyleneimine) dendrimer, 614
- Poly(propylene terephthalate), 201
- Polypyrrole, 618
- Polystyrene, 591, 592
- Poly(trimethylene terephthalate),
 - 201, 404
- Polyurethane, 242, 253, 420, 563, 609, 610
- Polyurethane foams, 609, 610
- Polyurethane foams, formation of, 610
- Polyurethanes, 606, 611
- Poly(vinyl acetate) film, 391
- Poly(*N*-vinylcarbazole), 619
- Poly(vinyl chloride), 260, 581
 - plasticizers for, 743
- Poly(vinyl chloride) (PVC), 509
 - epoxidized oils, 510
 - plasticizer, 510
- Poly(vinylidene chloride) films, 203
- p,p'*-Diaminodicyclohexylmethane, 292
- Propane
 - acrylonitrile, conversion of, 675
 - ammoxidation of, 469
 - aromatics yield from aromatization, 471
 - catalytic oxidation of, 469
 - dehydrogenation of, 470
 - dehydrogenation process technology, 127
- Propane dehydrogenation process
 - technology, 214, 215
- 1,3-Propanediol, 200
 - odd carbon effect, 200
- Propane–propylene mixture
 - chlorolysis of, 415
- Propionic acid, 186
 - synthesis, 186
 - use of, 186
- Propylene
 - ammoxidation of, 409
 - catalytic cracking provide, 133
 - export, 114
 - global propylene demand pattern, 213
 - hydroformylation of, 188
 - with isobutane, interaction of, 124
 - main polymers and chemicals from, 217
 - major chemicals from, 261–263
 - oligomerization of, 221–222
 - pipelines, 77
 - polymerization, 124
 - polymers and copolymers, 217–221
 - production, 448
 - by catalytic cracking, 115
 - and price ratios, 214
 - refinery grade, 212
 - supplies by source and region, 212
 - via enhanced fluidized catalytic
 - cracking, 215
 - via selective C_4/C_5 cracking, 215
 - yield from representative cracker
 - feedstocks, 213
- Propylene glycol ethers, 246

- Propylene oxide, 243
 applications, 253–255
 based on epoxidation of propylene by
 hydrogen peroxide (HPPO), 246
 preparation, 243
 process, developed by, 243
 Dow, 243
 Oxirane, 244
 processes, 247
 acetoxylation of propylene, 247, 248
 biotechnological approaches, 252–253
 direct oxidation, 249
 electrochemical processes, 250, 251
 use of peracids, 249, 250
tert-Butanol as by-product, 244
- 2-Propylheptanol, 260, 389
- Proteolytic enzymes, 661
- Proton exchange membrane fuel cell, 731
- Protonic ceramic fuel cells (PCFCs), 734
- Purified terephthalic acid (PTA), 399
- Pyridines, 189, 190, 477
- Pyrolysis gasoline, 90, 106, 108, 323, 325, 383, 471
- Pyromellitic dianhydride, 570
- Pyromellitic dianhydride (PMDA), 455
- Pyrrole, 618
- Radiofrequency identification (RFID)
 tags, 622
- Raney nickel catalyst, 420
- Rapeseed oil, 496
- REACH legislation, 32
- Reaction injection molding (RIM), 633
 compound, 130
 technology, 607
- Recycling rates, of materials, 754
- Registration, Evaluation and Authorization of
 Chemicals (REACH), 29
- Reliance Industries, 53
- Reserves-to-production ratios, 713
- Resoles, formation of, 607
- Rhodium, 257
- Rhodium catalysts, 158, 160
- Rhodium-catalyzed process, 441
- Rhodium chloride, 261
 dilute solution of, 658
- Rhone Poulenc, 56, 58, 258, 294, 346
- Riboflavin, 697
 industrial synthesis of, 697
- Ricinoleic acid
 with OH group, 510
 sodium/calcium salt, dry distillation
 of, 511
- Rigid foam products, 610
- Ritter reaction of isobutene with hydrogen
 cyanide, 300
- Roche process, 660
- Rosin, 501
- Rubber technology, 280
- Ruthenium dyes, for dye-sensitized solar
 cells, 724
- SABIC, 53, 106
- Sachsse process, 418
- Salicylic acid, formation of, 328
- Saponification
 yields allyl alcohol, 264
- Sasol
 catalyst, 157, 158
 copolymers of pentene-1 and, 321
 ethylene capacity, 53
 newest synthetic fuels technology, 459
- Saudi Arabia
 availability of ethane in, 112
 cheap ethylene converted to ethanol, 68
 ethane cracking, 112
 ethane production, 112
 ethylene production, 53
- Seawater, 745
- sec*-Butanol, 276, 302
- Selectivity
 to phenol, 330
 of propylene to propylene oxide, 245
- Seminal reaction, 433
- Sertraline, synthesis of, 695
- Sewage, tertiary treatment of, 752
- Shale gas, 100, 101
 C_2 + compounds, 102
 technology, 101, 102
 hydraulic fracturing, 101
- Shell Heigher Olefins Process (SHOP), 158
 C_4 – C_{10} and C_{16} – C_{40} α -olefins are
 isomerized to, 160
 C_{10} – C_{14} α -olefins, hydroformylated
 to, 158
 C_{10} – C_{14} products are separated by
 distillation, 158
 distillation, 160

- metathesis, olefins to provide, 160
- oligomerization of ethylene, 158
- Shell Middle Distillate Synthesis (SMDS), 460
- Shell Oil, 747
- Ship vetting, 86
 - categories governed by Joint Industry Developed Standard, 86
- SHOPprocess, 129
- Showa Denko process, 39, 58, 167, 264, 266, 441
- Silane hydrolyzes, 412
- Silica-alumina/platinized-alumina catalyst, 385
- Silicone resins, 412
- Silicones, 412
- Silver catalyst, 639
- Silver manganate catalyst, 470
- Single-site catalysts, 600, 603
- SI (Système international d'unités) system, 5
- Sludge, treatment of, 751
- Slurry polymerization, 580
- Soaps, 501
 - with hydrochloric acid, 501
- Sodium hydroxide, 410
- Sodium nitrilotriacetic acid, 409
- Sodium tripolyphosphate, 751
- Solar energy generating systems (SEGS), 721
- Solar energy, generation of electricity, 721
- Solazyme, 518
- Solid acid catalysts, 231
- Solid wastes, disposal of, 752
- Solid wood packaging
 - treatment of, 741
- Solvay process, 681
- Solvent-based coatings, 393
- Solvents, in polyurethane formulations, 193
- Soot-sulfate aerosols, 709
- Sorona®, 201
- South Korean, ethylene production in, 50
- Soybean oil, 391, 392
 - carbon-carbon double bonds, 609
- Square-cube law, 23
- Standard industrial classification (SIC), 13
- Steam cracking, 683
 - economics of, 110–114
 - of ethane and propane, 136
 - of ethane, propane, butane, naphtha, 212
 - furnace, 107
 - of liquid feedstocks, 323
 - mechanism of, 117–119
 - process using light liquid/gaseous feedstocks, 106
- Steam cracking of naphtha C₅ stream, 310
- Stereoregular polymers, 595
- Stereoregular polymer synthesis, 660
- Stress-strain curves, 630
- Stress-strain diagram, 629
- Strong sewage, 750
- Styrene, 177–181
- Styrene-acrylonitrile (SAN) polymer, 284
- Styrene-butadiene elastomers, 281–282
 - global elastomer consumption, 282
- Styrene-butadiene-styrene
 - block copolymers, 592
 - hydrogenated version, 592
- Styrene toxicity in polyester resins, 242
- Substitute natural gas (SNG), 428, 485, 488
- Sugar cane, photosynthesizer, 724
- SulClde, 60
- Sulfate aerosols, 747
- Sulfur-based impurities, 323
- Sulfur dioxide pollution, 746, 747
- Sulfur dioxide/smoke pollution, 746
- Sulfur hexafluoride, 709
- Sulfuric acid, 44
 - catalytica system, mechanism of, 466
- Sulfur, oxides of, 735
- Supercritical carbon dioxide., 686, 687
 - advantage of, 687
- Suspension polymerization, 582
- Sustainability, 707
 - climate change, 708–712
 - energy sources, 717
 - artificial photosynthesis, 724–726
 - concentrated solar power (CSP) installations, 721
 - dye-sensitized solar cells (DSSCs), 722–724
 - electric vehicles, 735–736
 - fuel cells, 729–735
 - hydrogen economy, 728–729
 - methane hydrate, 727–728
 - nuclear energy, 726–727
 - photovoltaic cells, 721–722
 - solar power, 721

Sustainability (*Continued*)

- wave power, 720
- wind power, 719
- pollution, 736
 - air pollution, 744
 - automobile exhaust emissions, 748–750
 - environmental problems, 759
 - nonpesticide lipophiles, 743–744
 - ozone layer, 738–741
 - pesticides, 742
 - petrochemical industry
 - wastes, 758–759
 - solid wastes, 752–753
 - combustion/incineration, 755–756
 - recycling, 754–755
 - sanitary landfill, 756–758
 - waste prevention, 753
 - sulfur dioxide particulates, 745–747
 - trace chemicals, 742
 - water treatment, 750–752
- resource depletion, 712
 - food, 713–714
 - people, 715–717
 - water, 714–715
 - valediction, 759–761
- Syndiotactic polypropylene, 605
- Syngas conversion, catalysts for, 674
- Synthesis gas production
 - global source, 425
 - reactions, 427
- Synthesis gas technology, 485
- Synthetic natural gas, 485
- t*-Amyl methyl ether (TAME), 297, 309
- t*-Butanol, used with methanol, 136
- Teflon, 205, 414
- Terephthalic acid (TPA), 398
- Terephthaloyl chloride, condensation of, 403
- tert*-amyl methyl ether (TAME), 309
- tert*-Butanol, 239, 244, 251, 299, 470
- tert*-Butylamine, for lubricating oil
 - additives, 301
- tert*-butyl hydroperoxide, 245
- Tertiary amines, 613
- Tetrabutylammonium chloride, 670
- Tetrachloroethylene (perchloroethylene), in
 - dry cleaning, 686
- Tetrachloromethane (carbon tetrachloride), 414
- Tetrafluoromethane, 709
- Tetrahydrofuran (THF), 421, 422, 423
- Tetrahydronaphthalene, 479
- Tetrahydrophthalic anhydride, use in
 - polyester, 293
- Tetralin, 484. *See also*
 - Tetrahydronaphthalene
- Thermoplastic, 629
- Thermoplastics soften, 562
- Thermoset polymer, useful in reaction
 - injection molding (RIM), 321
- Titanium dioxide–methylamine
 - hydrochloride acid waste, 696
- Titanium tetrachloride, 694
- Toluene
 - conversion entirely to *p*-xylene, 377
 - dinitrotoluene, 378–380
 - disproportionation, 376–377
 - end-use pattern, 376
 - global production, 375
 - hydrodealkylation of, 325
 - improvement developed by Mobil, 377
 - lesser volume chemicals from,
 - 380–382
 - benzaldehyde, 380
 - benzoic acid, 380, 381
 - benzyl acetate, 380
 - benzyl alcohol, 380, 381
 - benzyl chloride, 381
 - butyl benzoate, 381
 - p*-methylstyrene, 381
 - p*-tolualdehyde, 381
 - oxidation, 380
 - raising the octane number, 324, 325
 - in situ* hydrodealkylation, 375
 - interaction with 1,3,5-trimethylbenzene/
mesitylene, 377
 - variants of, 376–377
 - as solvent, 378
 - toluene diisocyanate, 378–380
 - transalkylation, 377
- Toluene diisocyanate (TDI), 608, 609
- Toluene hydrodealkylation, 429
- p*-Toluenesulfonic acid, 387, 660
- p*-Toluic acid catalyst, 649
- Toray process, 690
- Totally degradable plastic additive
 - (TDPA), 701
- Toxic equivalents (TEQs), 736

- Toxic Substances Control Act, 41
- Transport bed, 304
- Transporting chemicals
- cargo load, 85
 - common ethylene pipeline grid in Western Europe., 79
 - economic aspects, 87, 88
 - chemicals spot rates, 88
 - index for container freight, 87
 - shipping prices, 87
 - health and safety, 86, 87
 - International Maritime Organization guidelines, 86
 - standards and systems of labeling for chemicals, 87
 - voluntary labeling standard, 87
 - parcel tanker TMS Roland Essberger, 84
 - shipping chemicals, 75
 - gases, 75–77
 - liquids, 77, 79, 81–85
 - solids, 85, 86
 - shipping gas, 74, 75
 - shipping petroleum, 71, 73, 74
 - top shipping companies, 90, 91
 - trade in specific chemicals, 88–90
 - balance of trade, 88–90
- Trialkoxysilanes, 662
- Trichloroacetaldehyde
- in DDT manufacture, 190
- 1,1,2-Trichloroethane, 203
- Trichloroethylene, 423
- used as solvent and degreasing agent, 204
- Trichloromethane, 413, 414
- Triethanolamine, major application, 199
- Triethylammonium chloride, 688
- Triethylenediamine
- catalyst for interaction of isocyanates with polyols, 193
- Tri(2-ethylhexyl) trimellitate, 258
- Triglycerides, 493
- cocoa butter, 513
 - source of organic chemicals, 97
 - transesterification of, 513
- Trimellitic anhydride (TMA), 455
- Trimethylamine, 450
- Trimethylbenzylammonium hydroxide, 270
- Trimethylchlorosilane, 412
- 2,2,4-trimethylhexamethylenediamine, 242
- Trimethylhydroxysilane, 412
- Trimethylolethane, for alkyd resins and urethanes, 185
- Trimethylolpropane, 513
- 2,2,4-Trimethylpentene
- isomers, useful for gasoline pool, 276
- 2,4,4-trimethyl-2-pentene, 130
- Trinitrotoluene (TNT), 433
- Turkey-Red oil, 510
- Twitchell catalysts, 500
- UK coal industry, 491
- ULSD, production of, 746
- Utem, 338, 395
- Under-ground coal gasification (UCG), 488
- Union Carbide, 27, 56, 59, 156, 174, 256, 418, 455, 458, 469, 471
- United States
- acetylene-based processes, 419
 - balance of trade, 65
 - benzoic acid production, 328
 - bioethanol, renewable energy source, 555–556
 - butadiene's end-use pattern, 277
 - catalytic reforming, 99
 - chemical industry's propylene in, 133
 - Clean Air Act, 325
 - consumption of fats and oils, 496
 - cracker feedstocks, 103
 - ethyl chloride consumption in, 187
 - ethylene market, 102
 - ethylene production in, 50
 - ethylene, propylene, and benzene production, 140
 - as exporter of ethylene derivatives, 93
 - fats and oils, 497
 - for gasoline manufacture, 99
 - import of MTBE, 135
 - maleic anhydride consumption in, 305
 - organic chemicals industry, 49, 51
 - advantages, 63
 - patterns of oil consumption, 96
 - petrochemical ethanol, decline in production of, 68
 - phenolic resin production, 331
 - phthalate plasticizers, 389
 - polymers, 561, 562, 565
 - propylene production by catalytic cracking, 115
 - shale gas, 100

- United States (*Continued*)
 - sources of benzene in, 111
 - soybean oil, 496
 - synthetic acetic acid demand, 442
 - transport of petroleum, 75
 - waterways for chemicals, 79
- Units/conversion factors, 771–772
 - heat, 772
 - temperature, 772
 - weight/volume/pressure, 771
- Unleaded gasoline
 - advent of, 42
 - Clean Air Act, 131
 - contain nitrogen, 656
 - MTBE, 273
 - toluene and xylenes, 121
- Unsaturated polyesters resins, 393
- UOP processes
 - MX Sorbex process, 384
 - Pacol process, 470
 - Parex process, 384
- Uranium, 726, 727
- Urea, 434, 606
- Urea-formaldehyde (U/F) resins, 434
 - use for, 434
- Urea plants, 432
- Urethane (carbamate), 606
- Urethane technology, 193
- U.S. Toxic Substances Control Act, 29

- Vacuum forming, 635
- Vacuum gas oil (VCO)
- Van der Waals forces, 591, 624
- Vegetable oils, 498
- Vinyl acetate, 452
- Vinyl chloride, 160–164, 203, 489
- 4-Vinylcyclohexene, 290, 291
 - oxydehydrogenation of, 179
- Vinyl esters, 207, 208, 424
 - of fatty acids, used primarily, 208
 - preparation, 207
- Vinyl fluoride, 423
- Vinylidene chloride, 203
- Vinylidene fluoride, 204, 205
- Vinyl monomers, polymerization
 - of, 582
- Vitamin B₂ (riboflavin), 697
- Volatile organic compounds (VOCs), 393

- Wacker process, 234, 657, 658
- Waste
 - petrochemical industry, 758–759
 - recycling and reduction of, 758
- Waste management, 737
 - in chemical industry, 738
- Waste natural gas, 408
- Waste vegetable oil(WVO), 517
- Waterborne diseases, 714
- Water–gas conversion, 426
- Water pollution, 715. *See also* Pollution
- Water purification, 690
- Waterways Council Inc, 81
- Western Europe
 - cracker feedstocks, 103
 - demand for gasoline, 94
 - sources of benzene in, 111
- Western European trade balance of
 - petrochemicals derivatives, 67
- Westfield Slagging Gasifier, 487
- Wilkinson catalyst, 256
- Wilkinson complex, 646
- Wind power, 719
- Wöhler's reaction, 433
- World population, 718
- World Trade Organization (WTO), 114
- Wulff process, 418

- Xylenes
 - crystallization of, 383
 - C₈ stream
 - physical constants of, 384
 - hydrodealkylation of, 325
 - isomers, 383
 - raising the octane number, 324, 325
 - separations, world capacity for, 384
 - o*-xylene, 479
 - exothermic, 386
 - p*-xylene
 - isomerization of, 39
 - regional capacity, 397
 - thermodynamic yields of, 643
 - m*-xylenes, 384
 - ammoxidized, 400
 - isomerization of, 39
 - isophthalic acid, 395, 396
 - isophthalic acid, uses of, 395–397
 - nitrile, hydrogenation of, 395
 - o*-xylenes

- phthalic anhydride, 386
 - alkyd resins, 391–393
 - plasticizers, 387–391
 - unsaturated polyester resin, 393–395
- p*-xylenes
 - terephthalic acid/dimethyl terephthalate, 397
 - alternate sources for, 400
 - lower volume polymers, 403–404
 - oxidation of, 398–400
- 2,6-Xylenol (2,6-dimethylphenol), 343, 452
- Young's modulus, 628
- Zeolites, 115, 231
 - basic structural units, 665
 - catalytic effects of, 668
 - regeneration, 232
 - sodium aluminate and sodium silicate, 666
 - three-dimensional polymeric framework, 664
- Zeolite ZSM-5, 385
- Ziegler–Natta catalyst, 124, 191, 220, 303, 569, 572, 594, 595, 596, 599, 600, 604, 624, 641, 658
 - stereospecificity of, 595
- Ziegler–Natta polymerization, 601, 650
 - mechanism of, 598
 - use of, 598
- Ziegler–Natta polymers, 602
- Ziegler oligomerization
 - of ethylene, 155, 156
- Ziegler technology, 154
- Zinc oxide catalyst, 234, 426
- Zirconium phosphates, 116
- Zn–Cr catalyst system, 436
- ZSM-5, 666
 - catalytic effects of, 668
- Zyklon B
 - used by Nazis, 411